THE UNIVERSITY OF MICHIGAN
INDUSTRY PROGRAM OF THE COLLEGE OF ENGINEERING

A KINETIC STUDY OF THE ESTERIFICATION OF GLYCEROL WITH STEARIC, OLEIC AND LINOLEIC ACIDS

by

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NOMENCLATURE

a - initial concentration of acid, $\frac{\text{equivalents}}{\text{100 g mixture}}$

b - initial concentration of glycerol, $\frac{\text{equivalents OH}}{\text{100 g}}$

x - concentration of esterified product at any time, $\frac{\text{equivalents ester}}{\text{100 g}}$

$(a-x)$ - concentration of acid at any time, $\frac{\text{equivalents}}{\text{100 g}}$

$(b-x)$ - concentration of glycerol at any time, $\frac{\text{equivalents}}{\text{100 g}}$

t - time, minutes or hours (as indicated where used).

k, k_1, k_2 etc. - reaction rate constant, units may vary.

E_o - Activation Energy, $\frac{\text{calories}}{\text{gram mole}}$

A - Constant in Arrhenius equation, (collision factor), same units as k

T - Absolute temperature, °K.

R - Constant, 1.9865 $\frac{\text{calories}}{\text{gram mole }^\circ\text{K}}$

e - base for natural logarithms, 2.7183

α, β, γ - exponential constants

INTRODUCTION

The esters of glycerol were among the first esters synthesized by organic chemists. Over one hundred years ago Pelouze and Gelis (39) prepared a triglyceride from glycerol and butyric acid and thus demonstrated that glycerol and fatty acids would react to form esters and water. Since then many esterification reactions have been studied.

The number of esters that can be synthesized is practically infinite. For example, if all the sautrated, straight chain monocarboxylic acids having from one to twenty carbon atoms were reacted with all the saturated, straight chain primary alcohols having from one to twenty carbon atoms, a total of 400 esters would be obtained. Now, if all the possible unsaturated, branched chain, and polyfunctional alcohols and acids are considered, it is readily apparent that an enormously large number of esters can be synthesized.

Many kinetic studies have been made of simple esterifications. That is, the esterification of monofunctional alcohols and acids. Quite a few kinetic investigations have been made of the esterification of difunctional alcohols and acids. However, very little kinetic data is available on more complex esterification reactions.

The esters of glycerol and other polyfunctional alcohols have many important uses in the protective coating and other related industries. Fortunately, many of the glycerol esters can be obtained from natural sources, such as vegetable oils.

However, in many cases it is more desireable, because of the superior results obtained, to re-esterify glycerol with various fatty acids, rather than use the natural oils.

The esterification of glycerol has been investigated many times. But, in general, the goal of the investigations was to obtain a certain final product rather than study the kinetics of the esterification reaction.

The purpose of this investigation was to study the kinetics of the esterification of glycerol with stearic, oleic and linoleic acid as a function of temperature, degree of unsaturation of acids, and initial concentration of the reactants.

In order to do this, it was necessary to first purify commercial grades of stearic, oleic and linoleic acids using a rather elaborate technique. Therefore, this study consisted of two steps:

1. The separation of stearic, oleic and linoleic acids from commercially available fatty acid mixtures, and
2. A kinetic study of the esterification of these acids with glycerol. The main variables being temperature, initial concentration and degree of unsaturation of the acids.

I. HISTORICAL

Purification of Fatty Acids

The preparation of pure stearic, oleic or linoleic acids is a difficult task. Much study has been devoted to various methods of purifying these acids.

In general the purification has been accomplished by using one of the following general methods:

1. Preparation of derivatives of the acids which may be separated by physical processes, such as crystallization or distillation.
2. Purification of the acids by low temperature crystallization from various solvents.

In order for an acid derivative to aid in the purification of the acid, it must be possible to regenerate the acid from the derivative easily. One group of acid derivatives which may be easily changed back to the acid are the urea adducts. Urea will add to the acids in a methanol solution and then the acid can be regenerated upon the addition of water.

Urea adducts have been investigated extensively by Swern and Parker (53), who used this method chiefly to prepare oleic acid concentrates which could be purified further by other means. Swern and Parker found that the solubility properties of the urea adducts of stearic, oleic and linoleic acids were quite different. However, there were mutual solubilities of adducts in each other which prevented the complete separation of the adducts from each other by crystallization. Nevertheless, they were able to prepare oleic acid concentrates containing up to 95% oleic acid.

Essentially the method of Swern and Parker (53) for preparing oleic acid concentrates was as follows:

1. Prepare the urea adduct by adding urea to the acids in a methanol solution.
2. Crystallize at 0°C overnight.
3. Filter, saving the cake.
4. Regenerate the acid by adding water.
5. Distill the acid layer under a high vacuum.

Newey, Shokal, Mueller, Bradley and Fetterly (35) demonstrated that urea does not form complexes with linoleic or linolenic acids under the same conditions as oleic and more saturated acids do, therefore, the more saturated acids can be removed as complexes while the more unsaturated acids left in the raffinate. Thus removal of the solvent from the raffinate by distillation will leave an acid mixture containing a large proportion of highly unsaturated acids, while the adduct can be regenerated to obtain the more saturated acids.

Both Swern and Parker, and Newey et.al. point out that this technique does not permit the preparation of high purity acids but instead produces concentrates from low purity acid mixtures. That is, this technique can be used to upgrade a fatty acid mixture from, for examplt, 60% oleic acid to 90% oleic acid.

The preparation of pure stearic, oleic and linoleic by low temperature fractional crystallization has been studied for a number of years by J. B. Brown and co-workers at Ohio State University (7,8,9,10, 11,19,20,27,32,33,47,48). They have worked out techniques for the preparation of pure acids by taking advantage of the differences in solubilities of the acids in selected solvents. The following methods were proposed by Brown (7,8) for preparing pure stearic, oleic and linoleic acids:

Stearic acid

Cool a 5% solution of fatty acid mixture (preferably one containing more than 70% stearic acid) in acetone, methanol or petroleum ether to -20°C, filtering and washing the precipitated acids once or twice with fresh solvent cooled to -35 to -40°C. Brown (8) says it may be necessary to repeat the crystallization once or twice.

Oleic Acid

The spearation of pure oleic acid from olvie oil fatty acids was accomplished by the following procedure (7):

1. 22.5 g olive oil fatty acids were dissolved in 3450 ml acetone., cooled to -20°C and filtered.
2. The filtrate was then cooled to -60°C and filtered.
3. The crystals were then submitted to three crystal lizations at 60°C from 2 litus of acetone each time.
4. The crystals were then crystallized at -35°C from 1250 ml acetone.
5. The filtrate was then crystallized at - 60°C.
6. The residual solvent was then distilled off.

Iodine Value = 89.9 , M.P. = 13.3

Other similar techniques have been described by Brown et.al. (19,20) for the preparation of oleic acids from olive oil fatty acids. They all involve several steps and give a fairly good yield and a very high purity oleic acid. Brown (8) also gives a method for preparing pure methyl oleate from olive oil fatty acids. This ester can then be hydrolyzed to give pure oleic acid.

Linoleic Acid

Pure linoleic acid was obtained by Brown et. al. (8) from Safflower oil fatty acids as follows:

1. Dissolve 297 g Safflower oil fatty acids in 4 liters of acetone, cool to -32°C and filter.
2. Cool filtrate to -50°C, and filter.
3. Cool filtrate to -72°C and filter.
4. Dissolve 154 g cake in 2350 ml acetone, cool to -48°C and filter.
5. Dissolve 100 g cake in 1690 ml petroleum ether, cool to -48°C and filter.
6. Dissolve 55 g cake in 350 ml petroleum ether and cool to -62°C.
7. Recrystallize and distill off the solvent.

Iodine Value = 180.5 , M.P. = -5.0 to -4.8°C.

Brown (8) says this technique is satisfactory to prepare good-sized amounts of pure linoleic acid with those vegetable oils containing more than 50% linoleic acid.

Other methods of purifying fatty acids have been investigated, the most notable being chromatographic methods. However, none have produced pure fatty acids on a large enough scale to warrant consideration for this particular investigation.

Kinetics of Glycerol Esterification

The first synthetic glyceride was prepared by Pelouze and Gelis (39) in 1844. They prepared a triglyceride from glycerol and butyric acid. In 1853 M. Berthelot (2) reacted 18 carbon chain fatty acids with glycerol in sealed tubes. He found that if the water of the reaction was not removed an equilibrium was reached after the reaction was approximately 46% complete. In later work Berthelot (21) was able to prepare mono-and di-glycerides as well as triglycerides. However, he paid no attention to the kinetics of the reaction. Instead he concentrated on the determination of equilibrium compositions.

The first patent for the manufacture of triglycerides was issued in 1907 to F. Ulzer and J. Batik (54). Since that time many patents (21) have been issued for the manufacture of glycerides.

In 1929, Long, et.al. (30) prepared triglycerides of stearic and oleic acids in order to study their molecular dimensions with the aid of a Langmuir balance. They tell how the glycerides were prepared by removing the water of reaction with inert gas, and state that the acids were purified by the usual methods. But no indication was given of the purity of the acids or what any of their chemical or physical properties were. Furthermore, no mention is made of the kinetics of the reaction.

Goldsmith (21) presents an excellent review of the work done on the esterification of glycerol up to 1943. He lists numerous references of uncatalyzed esterifications as well as catalyzed esterifications. The investigators referred to by Goldsmith (21) were always interested in either the technique of making monoglycerides, diglycerides or triglycerides

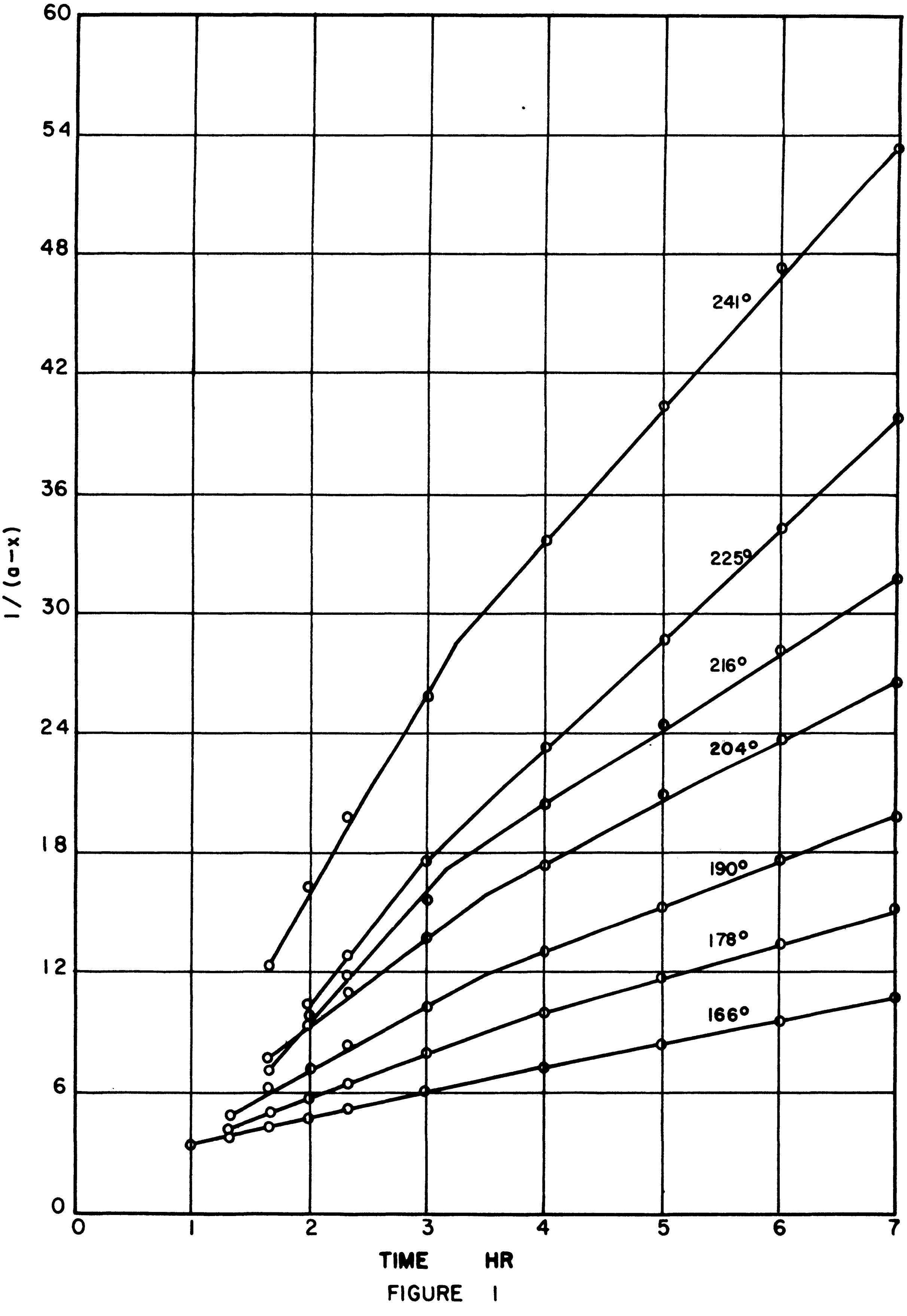


FIGURE 1

$\frac{1}{a-x}$ PLOTTED AGAINST t FROM DATA OF FEUGE, KRAEMER AND BAILEY (17) FOR THE REACTION BETWEEN PEANUT OIL FATTY ACIDS AND GLYCEROL or in how much the overall reaction time could be reduced by the use of catalysts.

Feuge, Kraemer and Bailey (17) made the first kinetic investigation of the formation of glycerol esters. They reacted glycerol with peanut oil fatty acids at temperatures ranging from 166° C to 241° C and at a pressure of 20 mm Hg with and without a catalyst. The uncatalyzed reaction was reported to be bimolecular and thus the reaction followed the familiar second order rate equation

$$-\frac{d(a-x)}{dt} = k(a-x)(b-x),$$

where $(a-x)$ = acid concentration

$(b-x)$ = glycerol concentration

t = time, hr.

k = constant

a, b = initial concentration of acid and glycerol respectively

x = amount reacted

which integrates to

$$k = \frac{1}{t}\left(\frac{1}{a-x} - \frac{1}{a}\right)$$

if the initial concentrations of alcohol and acid are equivalent. Therefore, if a plot of $\frac{1}{a-x}$ against t is made, a straight line with a slope equal to k should be obtained. Feuge, Kraemer and Bailey (17) found that the reaction gave two distinctly different straight lines when $\frac{1}{a-x}$ was plotted as a function of time. See Figure 1.

The initial part of the reaction gave a line with a steeper slope than the final part of the reaction. No concrete explanation of this phenomena was offered but instead it was reported that the initial slope might be an indication of how fast the primary hydroxyl groups of the glycerol molecule reacted, while the final slope might be an indication of how fast the secondary hydroxyl groups of the glycerol molecule reacted. No attempt was made to explain why the "break point" occurred at different $\frac{1}{a-x}$ values for each different temperature. It was apparent, although not mentioned, that the "break point" was not a linear function of temperature. This "non-linearity" was also noticed by the Northwestern Paint Production Club (36) in their work on the esterification of diglycerol with soybean oil fatty acids. Obviously, the "break points" did not occur at the $\frac{1}{a-x}$ value corresponding to 2/3 of the acid reacted, which should be the case if the reaction is the two step process mentioned above.

Feuge, Kraemer and Bailey (17) also correlated the reaction rate constant, k, for both the initial and final steps of the reaction, according to the classical Arrhenius equation

$$k = Ae^{-E_o/RT} .$$

It was found that both constants obeyed this law, and that the Activation Energy, E_o, was 12,300 cal/mole for the initial step and 10,800 cal/mole for the final step. The "collision factor", A, was 2.00×10^6 for the initial step and 2.77×10^5 for the final step. These values agree with other values of the activation energy of esterification reactions (16,25, 26).

They found further that increasing the pressure from 20 mm Hg to atmospheric pressure had essentially no effect on the reaction rate constants.

This reaction was also investigated in the presence of a number of catalysts and it was reported that the reaction remained bimolecular in the presence of numerous metal salts, except for zinc or tin chloride. These two catalysts seemed to change the mechanism of the reaction and increase the rate of the reaction tremendously. Feuge, Kraemer and Bailey made no attempt to correlate catalyst concentration with the reaction rate.

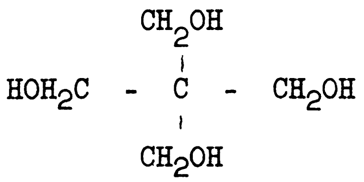
Burrell (12) and Konen, Clocker and Cox (28) studied the effect of catalysts on the overall reaction time of glycerol, pentaerythritol, erythritol and other polyhydric alcohols, with linseed oil fatty acids. Burrell concluded that calcium soaps increased the reaction rate, thus decreasing the reaction time. Konen, Clocker and Cox, on the other hand, found the catalysts to be effective only in the initial part of the reaction and that the overall reaction time was changed only slightly upon the addition of various catalysts.

The work of the Northwestern Production Club (36), mentioned earlier, was a comparison of two reactions. One was the esterification of glycerol with soybean oil fatty acids and the other was the esterification of diglycerol with soybean oil fatty acids. Diglycerol maybe produced by dehydrating glycerol in the presence of a catalyst and heat. It contains two primary hydroxy groups and two secondary hydroxy groups. The Northwestern Production Club reported that they could correlate their data in the same way that Feuge, Kraemer and Bailey did. However, they noticed that the "break point" for the reactions did not occur at the point where the reaction was 50% complete in the case of diglycerol or 67% complete in the case of glycerol. Instead its location varied non-linearly with temperature. Thus it was concluded that the "break point" was perhaps somehow related to the differences in reactivity between the primary and secondary groups of the glycerol molecule, but was not entirely due to these differences. Their data indicates that glycerol and diglycerol react at approximately the same overall rate but kinetic data is given only for the reaction between diglycerol and soybean fatty acids. No data is included on the activation energies of "collision factors" from an Arrhenius plot. Using their data a plot can be made of the reaction rate constants against 1/T for both the fast and slow steps of the reaction between diglycerol and soybean fatty acids. See Figure 2. Using the least squares method the slopes and intercepts were evaluated. The Activation energy is related to the slope by the equation

$$E_o = (\text{slope})(2.303R)$$

The Activation Energy for the fast step was found to be 14,528 cal/mole and for the slow step it was 12,300 cal/mole. The "collision factors" for the fast and slow steps respectively were 4.01×10^6 and 1.23×10^6. This agrees with Feuge, Kraemer and Bailey's (17) results and also other reported Activation Energies for fatty acid esterification (16,25,26).

Another kinetic study of the esterification of polyhydric alcohols with fatty acids is the investigation of Blagonravova and Lazarev (3). They reacted linseed oil fatty acids with pentaerithyritol, which has four hydroxyl groups:



$$\begin{array}{c} CH_2OH \\ | \\ HOH_2C - C - CH_2OH \\ | \\ CH_2OH \end{array}$$

Pentaerithyritol

They found that the reaction was bimolecular above 180°C, but that below 180°C it was no longer bimolecular. An activation energy of

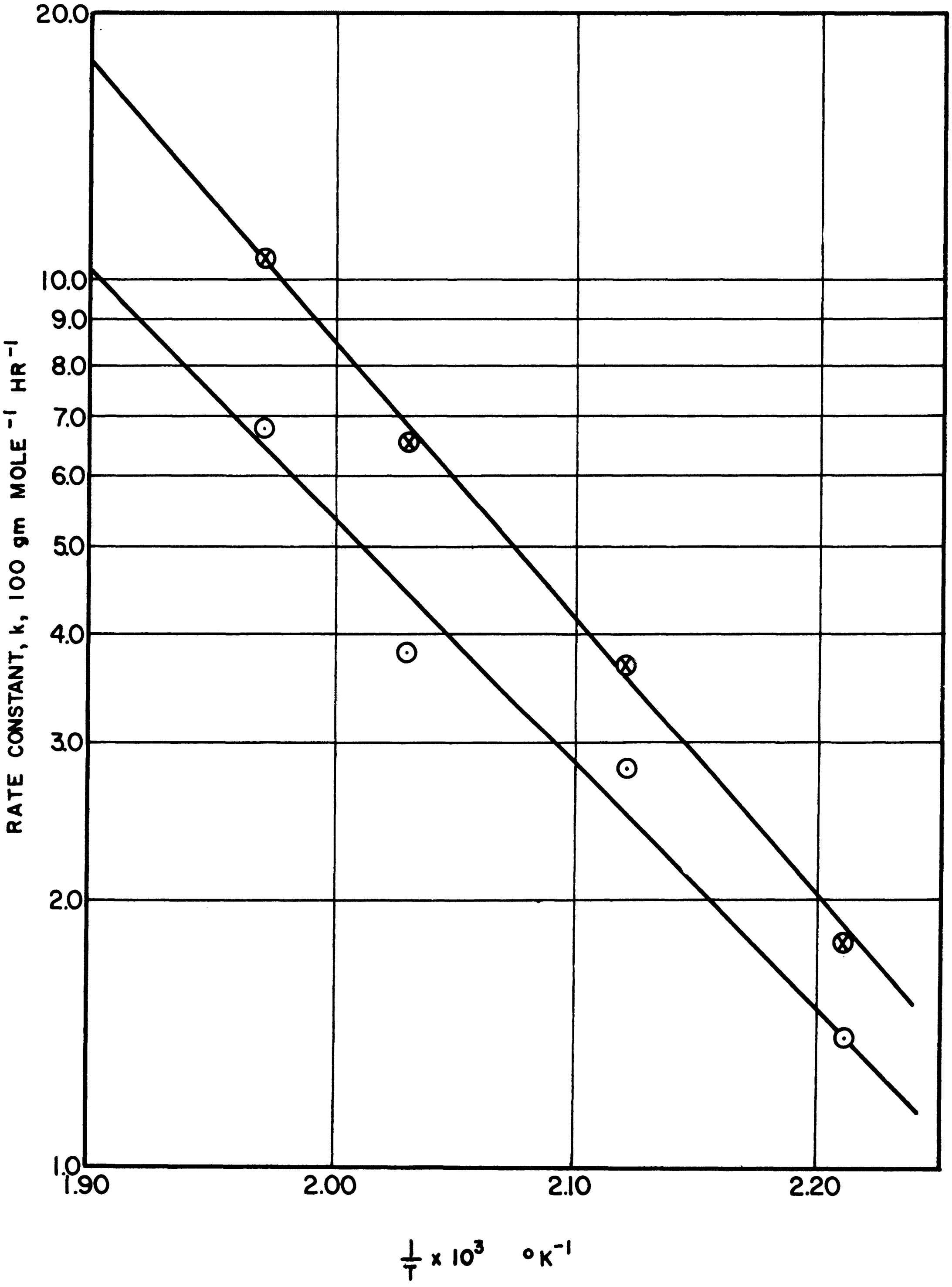


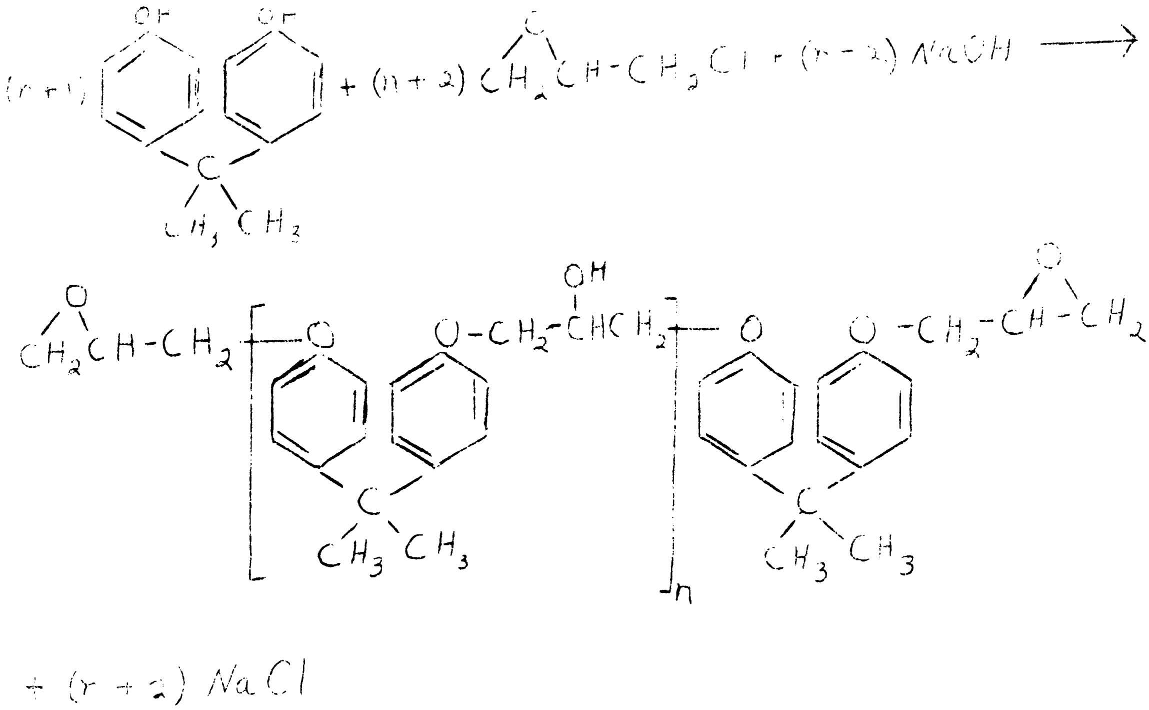
FIGURE 2 LOG k AS A FUNCTION OF $\frac{1}{T}$ FROM DATA OF NORTHWESTERN PRODUCTION CLUB FOR THE REACTION OF DIGLYCEROL WITH SOYBEAN OIL FATTY ACIDS

⊗ FAST STEP ⊙ SLOW STEP

10,652 cal/mol is reported which is claimed to be in agreement with Hinshelwood (26).

Rubin (44) also made a kinetic investigation of the esterification of fatty acids with polyhydric alcohols. He reacted linseed oil fatty acids and whale oil fatty acids with Epikote resins 1004 and 1007.

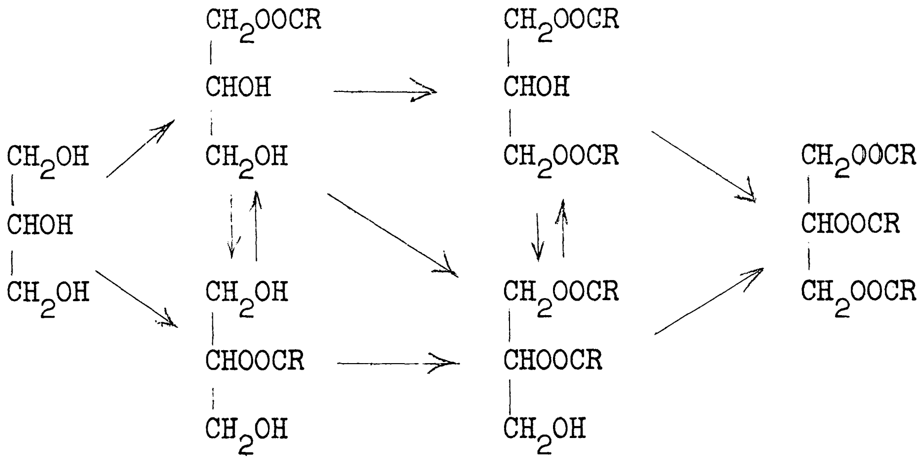
These resins are formed by the reaction of epichlor-hydrin and bisphenol in the presence of NaOH thus:



Rubin found the equivalent weights to be 215 gm per OH group for Epikote 1004 and 230 gm per OH group for Epikote 1007. The reaction was bimolecular, apparently, since the hydroxyl groups are relatively far apart and don't affect the reactivity of each other.

Brandner, Hunter, Brewster and Bonner (4) reacted linseed oil fatty acids with sorbitol, which has six hydroxyl groups. They found that the reaction obeyed first order kinetics except at the beginning and at the end of the reaction. The deviation at the beginning of the reaction was attributed to stearic effects. Rubin (44) states that this data was not treated properly from a kinetic standpoint, and this does appear to be true, although a critical interpretation of the data was not made.

Markley in his book "Fatty Acids" (31) proposes a mechanism for the formation of triglycerides as follows:



Neither Fuege, Kraemer, and Bailey (17) or the Northwestern Production Club (36) make any mention of a possible mechanism nor is any mention made of the reactions of interesterification where the secondary ester is rearranged to the primary ester or vice versa. These side reactions might conceivably have some effect on the reaction kinetics, but just exactly what can not be predicted.

Flory (18) states that polar groups on adjacent carbon atoms affect each others reactivity, and that this reactivity is unchanged throughout the reaction, even though one of the groups may react before the other. This means that the reactivity of the secondary hydroxyl group on the glycerol molecule does not change during the course of the reaction. This may indicate that the reasoning of Feuge et.al. and the Northwestern Production Club may be somewhat over simplified. That is, perhaps the reaction is not as selective as it may appear. It doesn't seem that an acid group would make a choice between a primary hydroxyl group and a secondary hydroxyl group if both were available. Instead, it appears that the laws of chance would rule in this case. Perhaps, up to now the data has not been correlated properly to give a true picture of what is happening.

II. APPARATUS AND PROCEDURES

Purification of Fatty Acids

The purification procedures recommended by Brown (7,8) were followed almost entirely because the starting materials were commercial grade stearic, oleic and linoleic acids, with one exception. The exception was that part of the linoleic acid was obtained from safflower oil fatty acids, and actually this was roughly equivalent to a commercial grade of linoleic acid. Thus, only materials containing a large percentage of the desired acid were used as starting materials.

Stearic Acid Preparation

Pure stearic acid was obtained from two different commercial grades of stearic acid:

1. Neo-Fat 18 from Armour and Company
   93% Stearic Acid*
   2% Oleic Acid
   5% Palmitic Acid
2. U.S.P. Stearic Acid from Merck & Co.
   The composition was not known, but it had an Iodine Value of 5 - 6 and a melting point of 59.5°C.

The following procedure was used to prepare pure stearic acid from these materials:

1. 12 g of the acid were dissolved in 1000 ml of acetone, cooled to -20°C and held for a minimum of

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* Typical analysis as furnished by Armour and Company Publication "The Chemistry of Fatty Acids".

of 4 to 6 hours then filtered and washed with cold acetone.(-20°C).

2. The crystals obtained were subjected to two more identical crystallizations.
3. The crystals obtained from the third crystallization were spread out on a piece of paper and dried in an oven at 120°F to remove the residual acetone.

An analysis of the crystals yielded an Iodine Value of 0.0 and a m.p. = 69.4 to 69.6°C. A sample of pure stearic acid obtained from The Hormel Institute, Austin, Minnesota had an I.V. = 0.0 and a m.p. = 69.5 to 69.7°C. The theoretical melting point is 69.4°C (22). Thus the stearic acid prepared had a purity of 99.9 + % based on this comparison.

The crystallization flasks were wide mouth "mason" jars which were covered with regular jar lids during the crystallization period. The cold box for the crystallization process was a commerical deep freezer which could be set at -20°C and had an operating range of ± 2°C.

The filtration of the crystals was carried out at room temperature, since the only adverse effect was that a slight amount of stearic acid would be redissolved. It was found that this redissolution was very minor and could be ignored. The filtration apparatus consisted of a 5 liter filtration flask with a suction connection connected to a vacuum pump. The filtration funnel was an 18 cm diameter procelain Buechner funnel with a perforated plate. Regular 18 cm filter paper was used to collect the crystals.

The Iodine Value (I.V.), which is a measure of unsaturation, was determined using the method of Mukherjee (34). This method is considerably faster than the usual methods of determining the I.V. (Wijs or Kaufmann) and it also eliminates the need for completely anhydrous reagents. Mukherjee (34) gave a large amount of data to demonstrate that his method is as accurate as the Wijs or Kaufmann methods. The theoretical Iodine Value for a completely saturated material such as stearic acid is 0.0.

The melting points were measured by the standard capillary tube method. A thermometer calibrated by the National Bureau of Standards was used to check the melting points.

Oleic Acid Preparation

Pure oleic acid was obtained from a commercial grade of oleic acid, Emersol 233 LL Elaine, furnished by Emery Industries, Inc. The composition of a typical batch of this oleic acid was:*

87%	Oleic Acid
4%	Linoleic Acid
3%	Myristic Acid
6%	Palmitic Acid

The procedure outlined by Brown (7) was used in a modified form to purify this acid. The modified procedure was as follows:

1. Dissolve the impure acid in acetone, 100 g/liter, cool to -20°C overnight and filter.
2. Cool the filtrate from step 1 to -60°C and filter.

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* From Emery Publication, "Emersol Oleic Acids".

3. Dissolve the crystals from step 2 in acetone, 200 g/liter, cool to -35°C and filter. Wash the crystals with cold acetone (-35°C) adding the washings to the filtrate.
4. Cool the filtrate from step 3 to -60°C and filter.
5. Dissolve the crystals from step 4 in acetone, 60 g/liter, cool to -35°C and filter.
6. Cool the filtrate from step 5 to -60°C and filter. Save the crystals.
7. Remove the residual solvent from the pure oleic acid by heating the acid and acetone rapidly to 70°C over a steam bath.

An analysis of the oleic acid obtained yielded an I.V. of 89.8 and a m.p. of 13.0°C as compared to a theoretical I.V. of 89.9 and a theoretical m.p. of 14°C (22). A sample of 99.3% oleic acid obtained from the Hormel Institute had an I.V. of 89.8 according to their measurements. The writer found the I.V. was 89.7 and the m.p. was 13.1°C. This indicates that the oleic acid obtained by the above procedure was more than 99% pure.

The Iodine Value and the melting point were obtained in the same manner as described in the section on the preparation of pure stearic acid.

The "mason" jars were again used as crystallization flasks. In order to obtain the low temperatures required the use of an Anerican Instrument Company Sub-Zero Test Cabinet. This cabinet contained a chamber for dry ice, a fan to flow air over the dry ice, and a thermostat to shut the fan off when the desired temperature was reached. The temperature inside this cabinet could be controlled with + 1°C by means of the thermostat and a damper in front of the fan. The storage space was a cube approximately 2 ft. on a side.

The filtration of the crystals which had been cooled to -20°C was conducted with the filtration apparatus at room temperature. However, for the filtrations of material crystallized out below -20°C it was necessary to chill the filtration flask and filtration funnel in the cold box, before the filtrations could be made. After the filtration apparatus was once chilled it could be used in the room outside the cold box, since the cold solvent and cold crystals kept it cold.

It was found that the filtration temperature could be kept one or two degrees above the crystallization temperature by this technique.

The filtration apparatus was the same as that used in the purification of stearic acid.

Linoleic Acid Preparation

It was not possible to obtain pure linoleic acid using the method recommended by Brown (8) and Frankel and Brown (20). Instead a purity of approximately 95% was obtained. After due consideration it was decided to use this material since it appeared that the main impurity was oleic acid.

Two different starting materials were used:

1. Emersol 9315, a commercial grade of Linoleic Acid, from Emery Industries, Inc.

   62% Linoleic Acid*

   28% Oleic Acid

   6% Linolenic Acid

   3% Palmitic Acid

   1% Myristic Acid

2. Safflower Oil Fatty Acids from Pacific Vegetable Oil Company.

   67.4% Linoleic Acid**

   26.4% Oleic Acid

   0.2% Linolenic Acid

   3.9% Palmitic Acid

   2.5% Stearic Acid

   0.6% Other fatty acids.

As stated above the procedure outlined by Brown (8) and Frankel and Brown (20) was followed almost exclusively without obtaining pure linoleic acid. The purification procedure was as follows:

1. Dissolve the fatty acids in acetone, 75 g/liter, cool to -20°C and filter.
2. Cool the filtrate from step 1 to -50°C and filter.
3. Cool the filtrate from step 2 to -70°C and filter.

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* Typical Analysis from Emery Industries Publication, "Average Composition of and Characteristics of Emery Fatty Acids".

**Typical Analysis from Archer-Daniels-Midland Co., "Fatty Acid Chart".

4. Dissolve crystals from step 3 in petroleum ether, 60 g/liter, cool to -61°C and filter. Save the crystals.
5. Repeat step 4 two or three times.
6. Remove the residual solvent by rapid heating to 70°C over a steam bath.

The I.V. of the material was 175-176 as compared to a theoretical I.V. of 180. A sample of linoleic acid obtained from the Hormel Institute had an I.V. of 179.

This material was analyzed further with a Beckman Ultra Violet Spectrophotometer according to the procedure outlined by Brice et.al (5,6) and Official Methods of the Am. Oil Chemists' Soc. (38). This analysis revealed that there were only 0.003% non-conjugated triple bond fatty acids present, and no conjugated triple bond fatty acids present. Thus the only acid which was contaminating the linoleic acid was oleic acid. The above analyses indicate that the linoleic acid content was in excess of 95%. Since the only impurity was oleic acid this acid was used without further purification.

The analyses and apparatus used for this purification other than the Ultra Violet analysis, were the same as described previously.

Glycerol Purification

The glycerol used in this study was synthetic glycerol manufactured by the Shell Chemical Company. The Company claimed that it had a purity of 99.7%. A check on the glycerol purity was run by another student in connection with another investigation and it was determined that the glycerol purity was greater than 99.6%. Therefore, no further purification of the glycerol was necessary for this investigation.

Esterification Apparatus

Figure 3 is a picture of the assembled esterification apparatus while Figure 4 is a picture of the apparatus with the constant temperature bath and heaters removed.

The constant temperature bath consisted of a 12" diameter, 10" deep glass jar inside a steel box. Between the jar and box there was one inch of insulation. The heating medium was Dow Corning 710 Fluid and it was heated by two electric immersion heaters, 250 and 750 watts, connected in parallel. The temperature of the bath was controlled by a Fenwal Thermoswitch. It was found that with this setup the temperature inside the reaction flask could be controlled within $\pm 1^{o}C$.

The reaction flask consisted of a 3-neck 500 ml flask with interchangeable ground glass fittings. Inserted through the center neck was a stirring rod with a stirring blade attached. The curvature of the stirring blade was the same as the curvature of the flask. The ground glass stirring rod was sealed by a ground glass adapter. By greasing the stirring rod with Dow Corning Stop Cock Grease, friction was eliminated and loss of reactants around the stirring rod was reduced to a minimum. The stirrer was driven by a variable speed Kenmore mixer motor. Throughout this investigation the stirrer speed was kept constant at 375 revolutions per minute.

Through one of the two remaining necks nitrogen gas was passed into the reaction mixture at a rate of 0.01 ft^3/min as measured by a

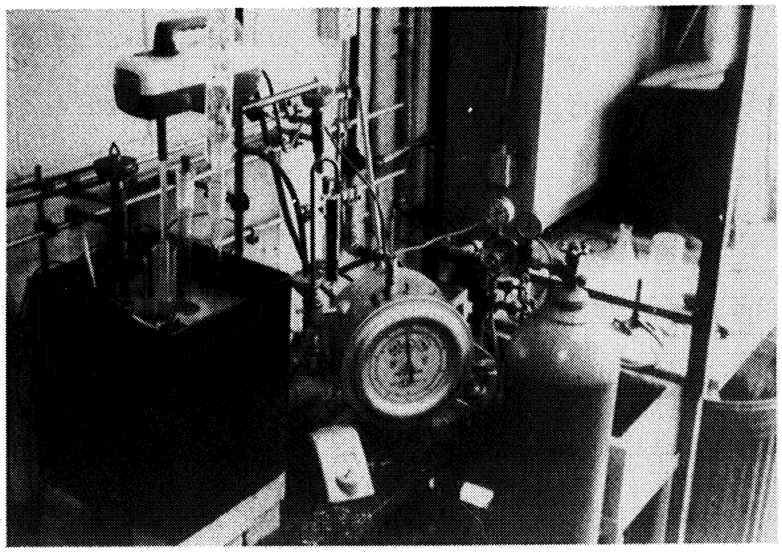


Figure 3. Assembled Esterification Apparatus

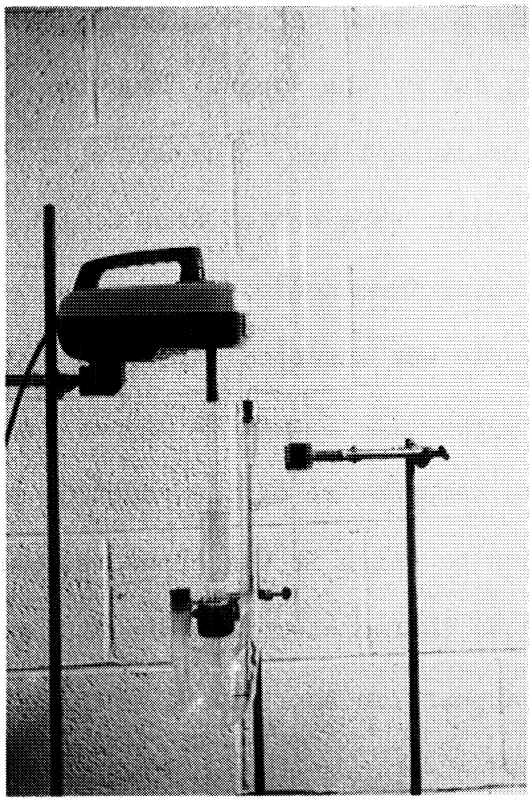


Figure 4. Esterification Apparatus with Constant Temperature Bath and Heaters Removed

Wet Gas Meter. The nitrogen gas was first bubbled through concentrated sulfuric acid to remove any oxygen and water in it. The inert nitrogen gas served two purposes:

1. It helped remove the water of reaction and thus prevented the reaction from reaching the equilibrium point between reactions products and reactants.
2. By creating an outward flow of inert gas, oxidation and darkening of the reaction mixture was reduced to a minimum. This was particularly important for the unsaturated acids.

A condenser, a water trap and a thermocouple were connected to the other neck of the flask. The water trap forced the vapor from the reaction mixture to turn a corner before entering the condenser where the water was condensed out of the vapor. Thus the water was prevented from returning to the reaction flask. The walls of the water trap, before the bend in vapor path, were heated from time to time with a bunsen burner to prevent the water from condensing before reaching the condenser.

The thermocouple was inserted through an opening in the water trap directly above the reaction flask. A copper-constantan thermocouple was used to measure the temperature of the reaction mixture. The thermocouple and potentiometer to which it was connected were calibrated as a unit against a calibrated thermometer from the National Bureau of Standards. The calibration curve appears in Appendix A.

Esterification Procedure

The esterification reactions were carried out according to the following procedure:

1. The constant temperature bath was heated to the desired temperature.
2. The acid was added to the reaction flask by removing the gas sparger and pouring the acid through this opening. Stearic acid had to be melted prior to putting it in the reaction flask.
3. After the acid had reached the reaction temperature, the glycerol was heated slightly above the reaction temperature in a separate flask over a bunsen burner. The glycerol was then added to the acid, and the stirrer and the timer were started.
4. The amount of acid or glycerol added to the flask was determined by accurately weighing (within 0.01 gram) the flask containing the acid or glycerol before and after the acid or glycerol was added to the reaction flask. That is, the weight of the flask plus the acid minus the weight of the empty flask after the acid was poured out was taken as the amount of acid added to the reaction flask.
5. Samples were removed for analysis whenever desired by a 2 ml syringe with a 6" #20 needle which was inserted through the cork which held the gas sparger in place.
6. The samples were then placed in small stoppered bottles and cooled rapidly to room temperature under the cold water tap.

The course of the reaction could be followed several ways:

1. Measuring the amount of water collected as a function of time.

2. Analyzing the samples removed for free hydroxyl (-OH) content.
3. Analyzing the samples removed for free acid (-COOH) content.
4. Analyzing the samples removed for free glycerol, monoglyceride, diglyceride and triglyceride content.

Measuring the amount of water collected is easily done by putting volume marks at different levels in the water trap. The water trap used was already so marked by the manufacturer. This is not a very accurate measurement because of the hold-up time of the water in the apparatus. The hold-up time was undoubtedly several seconds because the water had to get out of the reaction mixture, into the condenser and then into the water trap. Also, the accuracy of the graduated markings on the collection trap was not known. Thus this measurement was used only for qualitative estimates of how the reaction was progressing.

The analysis for free hydroxyl groups is relatively difficult when compared to the analysis for free acid groups. The analysis for free acid (38) can be made by a simple titration of the sample against a standard base solution such as KOH or NaOH. On the other hand, the analysis for free hydroxyl groups (38) requires several hours of refluxing followed by two titrations, one of the untreated sample and one of the treated sample. Thus it is easy to see that many more errors are possible in measuring the hydroxyl content than in measuring the acid content. Besides, if the initial concentrations are known, the free hydroxyl content can always be determined by a measurement of the free acid content.

The analysis for free glycerol, monoglycerides, diglycerides and triglycerides is very complex and difficult. Furthermore large samples (5-15 grams) are required for this analysis. This meant that in order to analyze for these constituents a large batch (2000-3000 gm) must be used. This fact, coupled with the lengthy purification techniques required to obtain small amounts of the pure fatty acids, made this analysis impracticable.

Thus the only analysis made on the samples was an analysis of the free acid content. A description of this technique is given in the next section.

Analysis of Samples

The samples were analyzed for free acid content by dissolving a weighed portion in 50 ml of a 50-50 mixture by volume of benzene and methanol (both C.P. grades) previously titrated with 0.1N KOH in methanol to a pink color with phenolphthalein indicator. The dissolved sample was then titrated to a phenolphthalein endpoint with 0.1 N KOH in methanol.

The number of ml of 0.1 N KOH solution used per gram of sample could be converted to the number of equivalents of free acid per 100 grams of mixture merely by dividing by 100. Proof of this is as follows:

$$\left(\frac{\text{liters } 0.1 \text{ N KOH}}{\text{g sample}}\right) \times (\text{Normality of KOH}) = \frac{\text{eq. KOH}}{\text{g sample}} = \frac{\text{eq. Acid}}{\text{g sample}}$$

and

$$\left(\frac{\frac{\text{ml } 0.1 \text{ N KOH}}{1000}}{\text{g sample}}\right) \times 100 \times \left(\frac{1}{10} \text{ Normal KOH}\right) = \frac{\text{eq. KOH}}{100 \text{ g sample}} = \frac{\text{eq. Acid}}{100 \text{ g sample}}$$

so

$$\frac{\text{ml } 0.1 \text{ N KOH}}{\text{g sample}} \times \frac{1}{100} = \frac{\text{eq. Acid}}{100 \text{ g sample}}$$

The samples were weighed on a regular chain-o-matic chemical balance with calibrated weights. The titrations were made with a calibrated automatic filling burette.

III. RESULTS AND DISCUSSION

In view of the fact that Feuge, Kraemer and Bailey (17) and The Northwestern Production Club (36) had found the esterification of glycerol followed a two-step mechanism when equivalent amounts of fatty acid and glycerol were reacted together, it was decided to determine if the second step could be eliminated entirely or postponed by using a large excess of glycerol. With this goal in mind the first reaction studied was between oleic acid and glycerol at 218°C using 50% equivalent excess of glycerol. Theoretically, then, only two hydroxyl groups on each glycerol would be esterified. Of course this may not be the case, but such selectivity appears to occur to a limited extent if the two step mechanism found by Feuge et. al. (17) and the Northwestern Production Club (36) is assumed to be correct.

For the esterification reaction where $a \neq b$, where a is the initial concentration of acid and b is the initial concentration of glycerol (eq/100 gm), the expression relating the reaction rate and the concentration of acid and glycerol, assuming the reaction is bimolecular, is

$$- \frac{d(a-x)}{dt} = k(a-x)(b-x). \qquad (1)$$

This in turn integrates to

$$k = \frac{2.303}{(b-a)t} \log \frac{a}{b} \frac{(b-x)}{(a-x)}$$

if $a \neq b$. Thus a plot of $\log \frac{(b-x)}{(a-x)}$ against t should produce a straight line with a slope proportional to k if the assumed relationship is valid.

Figure 5 is a plot of $\log \frac{(b-x)}{(a-x)}$ against t for the reaction between oleic acid and glycerol at 218°C using 50% equivalent excess

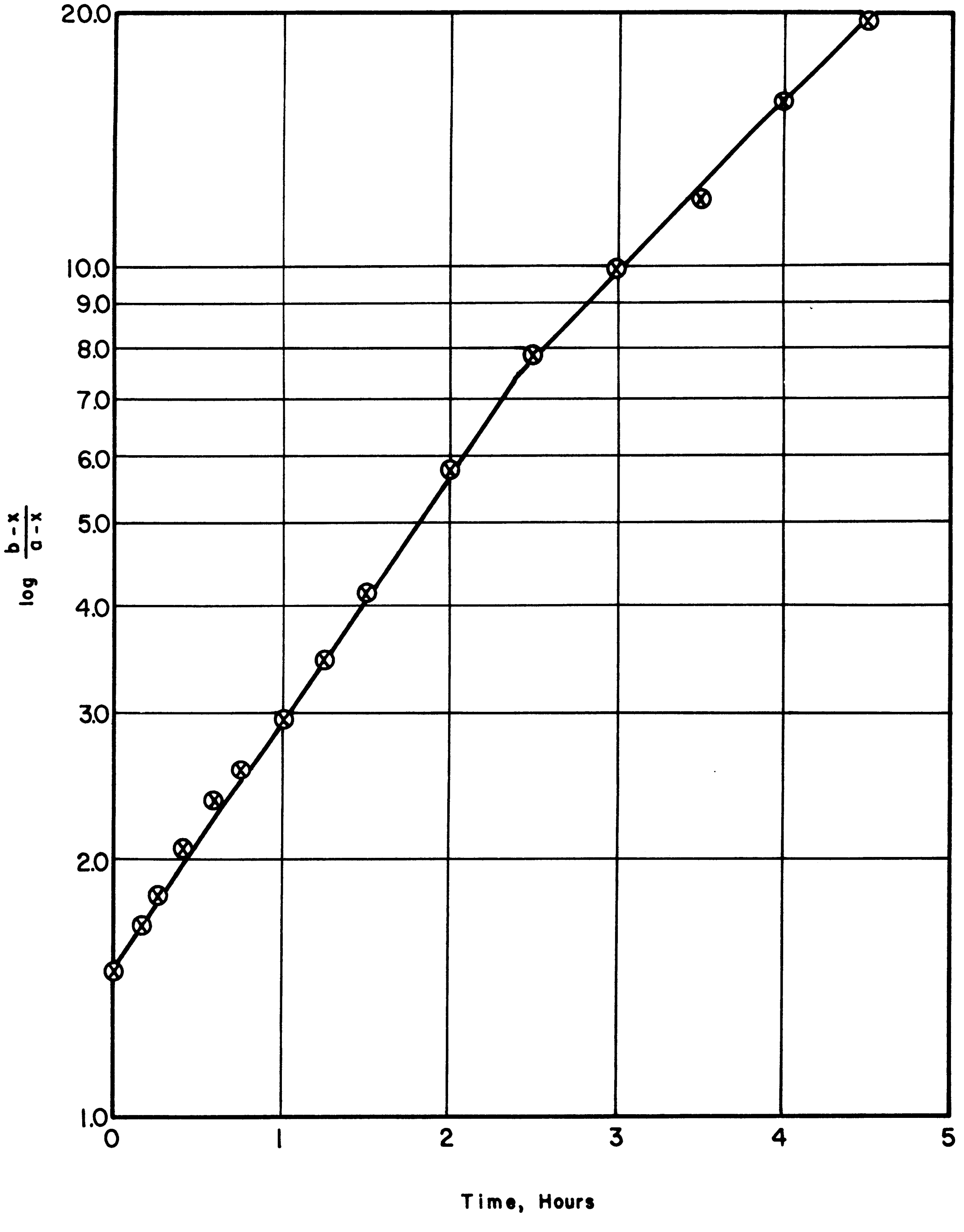


FIGURE 5

PLOT OF LOG $\frac{b-x}{a-x}$ AGAINST t FOR THE REACTION BETWEEN OLEIC ACID AND GLYCEROL AT 218° C, USING 50% EQUIVALENT EXCESS OF GLYCEROL

glycerol. Notice that the two step mechanism found by Feuge et.al. (17) is still indicated. However, the "break point" has been postponed until just after 90% of the acid has been reacted. Feuge et.al. (17) ran a reaction at 216°C using equivalent amounts of glycerol and peanut oil fatty acids and found the break point occurred just after 80% of the acid had been reacted. Thus from this comparison it appears that the break point apparently was not postponed very much by using a large excess of glycerol.

In order to determine just how much the break had been postponed, another reaction was run at 218°C between oleic acid and glycerol using approximately equivalent amounts. Actually, a 7% equivalent excess of glycerol was used. This was due to the fact that it was hard to determine just how much residual glycerol and acid would remain in the flasks used to put them into the reaction flask. Therefore, it was only after much experience that exactly the desired amount of glycerol and acid could be added to the reaction flask. Nevertheless, good approximations could be made right from the beginning.

Figure 6 is a plot of log $\frac{b-x}{a-x}$ against t for the reaction between oleic acid and glycerol at 218°C using a 7% equivalent excess of glycerol. Notice that the "break point" occurs much sooner than in the reaction using 50% equivalent excess glycerol. It occurs at 62 minutes after 70% of the acid has been reacted. So apparently the second step of the reaction may have some relationship to a reactivity difference between the different hydroxyl groups on the glycerol molecule. But this is not necessarily true because as indicated by Feuge, et.al (17) and the Northwestern Production Club (36) the break point also changes with temperature.

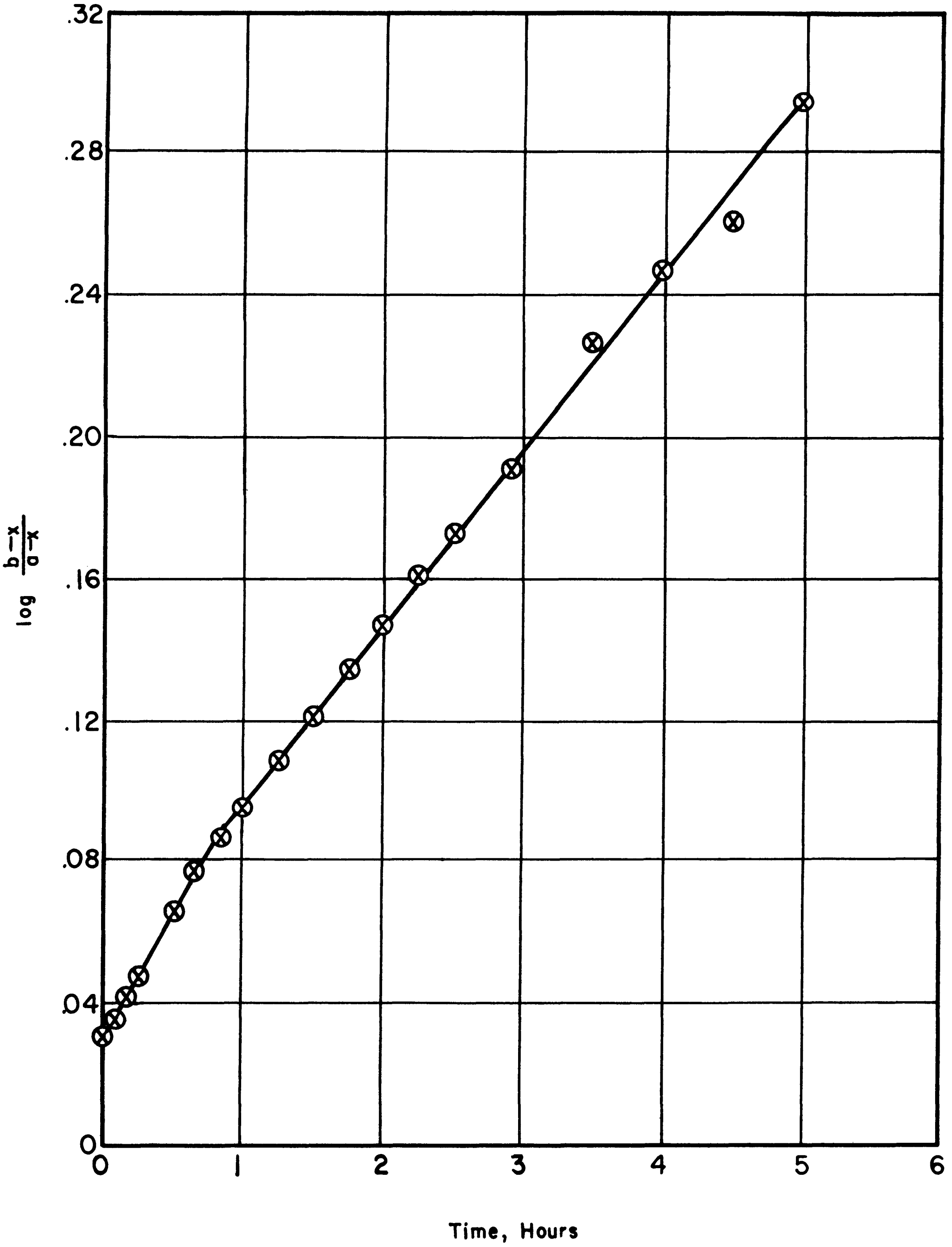


FIGURE 6

PLOT OF LOG $\frac{b-x}{a-x}$ AGAINST t FOR THE REACTION BETWEEN OLEIC ACID AND GLYCEROL AT 218° C USING 7% EQUIVALENT EXCESS GLYCEROL

Next the slopes of these lines were evaluated. If $\log \frac{b-x}{a-x}$ is plotted against t, then

$$k = \frac{2.303}{b-a} \text{ (slope).}$$

The calculated k values for the initial steps are as follows:

$k = 0.0742$ 50% equivalent excess glycerol, $\frac{a}{b} = 0.6676$

$k = 0.1065$ 7% equivalent excess glycerol, $\frac{a}{b} = 0.9313$

and for the second step:

$k = 0.0509$ 50% equivalent excess glycerol, $\frac{a}{b} = 0.6676$

$k = 0.0829$ 7% equivalent excess glycerol, $\frac{a}{b} = 0.9313$

Obviously, the assumed relationship

$$-\frac{d(a-x)}{dt} = k\,(a-x)(b-x)$$

must have been in error since the value of k seemed to depend upon the ratio of the initial concentration of acid to the initial concentration of glycerol, $\frac{a}{b}$. In order to check this apparent discrepancy two more reactions between oleic acid and glycerol were run. Both reactions were run at 199°C, the first having an equivalent glycerol excess of 51% and the second having an equivalent glycerol excess of 4%.

Once again upon plotting $\log \frac{(b-x)}{(a-x)}$ against t, the two step process was indicated. The "break point" for the reaction with 51% equivalent excess glycerol occurred after 68% of the acid had reacted. For the reaction with only 4% equivalent excess glycerol the "break point" occurred after 58% of the acid had reacted, thus indicating that the "break point" was also a function of temperature as had been indicated by the data of both Feuge, Kraemer and Bailey (17) and the Northwestern

Production Club (36).

Once again the k values were calculated from the slopes of the straight lines. These are as follows:

For the initial step,

$k = 0.0446$ 51% equivalent excess glycerol, $\frac{a}{b} = 0.6600$

$k = 0.0685$ 4% equivalent excess glycerol, $\frac{a}{b} = 0.9567$

and for the second step,

$k = 0.0333$ 51% equivalent excess glycerol, $\frac{a}{b} = 0.6600$

$k = 0.0536$ 4% equivalent excess glycerol, $\frac{a}{b} = 0.9567$

Thus once again it was apparent that the assumed relationship Eq. (1) was not valid since the reaction rate constant, k, varied as the ratios of initial concentrations of the reactants $\frac{a}{b}$, varied.

Listed in Table 1 is a comparison between the initial concentrations of the acid and glycerol and the reaction rate constants in the above four reactions.

Looking at Table 1, it may be seen that the initial concentration of glycerol varies much more than the initial concentration of the acid. This is due to the fact that the equivalent weight of oleic acid is 282.44 while the equivalent weight of glycerol is 30.70. Thus, a small change in the weight of glycerol added will change the equivalent glycerol concentration by a large amount, without changing the total weight of the reaction mixture or the acid concentration appreciably.

Since Equation (1) was apparently not valid it was decided to see if a more general form of the rate equation could be used to correlate the data. The general rate expression can be written (29):

Table 1

Initial Concentration of Oleic Acid and Glycerol in Reactions at 199°C and 218°C Compared to Reaction Rate Constants Obtained Using Correlation of Feuge, Kraemer and Bailey (17)

Temp. °C	a Initial Acid Conc. Eq. per 100 gm.	b Initial Glycerol Conc. Eq. per 100 gm.	$\frac{a}{b}$	k_1 rate constant for initial step	k_2 rate constant for final step
199	0.3040	0.4606	0.6600	0.0446	0.0333
199	0.3179	.3323	.9567	.0685	.0536
218	0.3045	.4561	.6676	.0742	.0509
218	0.3170	.3404	.9313	.1065	.0829

$$-\frac{d(a-x)}{dt} = \frac{dx}{dt} = k_o(a-x)^{\alpha}(b-x)^{\beta} \qquad (2)$$

In this equation there are three constants to be evaluated and, in order to evaluate them the instantaneous rate of the reaction, $\frac{dx}{dt}$ or $-\frac{d(a-x)}{dt}$, must be known. The rate may be determined by either of two methods:

1. Measure the slope of a plot of the concentration of acid against time at different points on the curve or,
2. Smooth the data by the use of a difference plot.

The measurement of slopes is not very accurate because of the difficulty encountered in drawing a tangent to any one point on a curve. Smoothing the data by the use of a difference plot is somewhat more accurate and is slightly easier than determining slopes.

A difference plot consists of plotting $\frac{\Delta(a-x)}{\Delta t}$ against t for each of the time intervals between samples. This produces a set of finite steps or plateaus, through which a smooth curve may be drawn. The curve should be drawn so that the area between the curves and the steps is equal to the area between the steps and curve. Figure 7 represents the difference plot for the reaction between oleic acid and glycerol at 218°C with 50% equivalent excess glycerol being used. The instantaneous rate, $-\frac{d(a-x)}{dt}$ at any time during the reaction can be determined from this plot.

The exponential constants, α and β, may then be determined by the following technique:

1. Determine the reaction rate, $-\frac{d(a-x)}{dt}$, at four points during the reaction at which the acid concentration (a-x) has been measured.
2. From the initial values of the acid concentration, a, and the glycerol concentration, b, the glycerol concentration at these four points, (b-x) can also be determined. That is:

$$(b-x) = b - \left[(a - (a-x)\right]$$

or

$$x = a - (a-x)$$

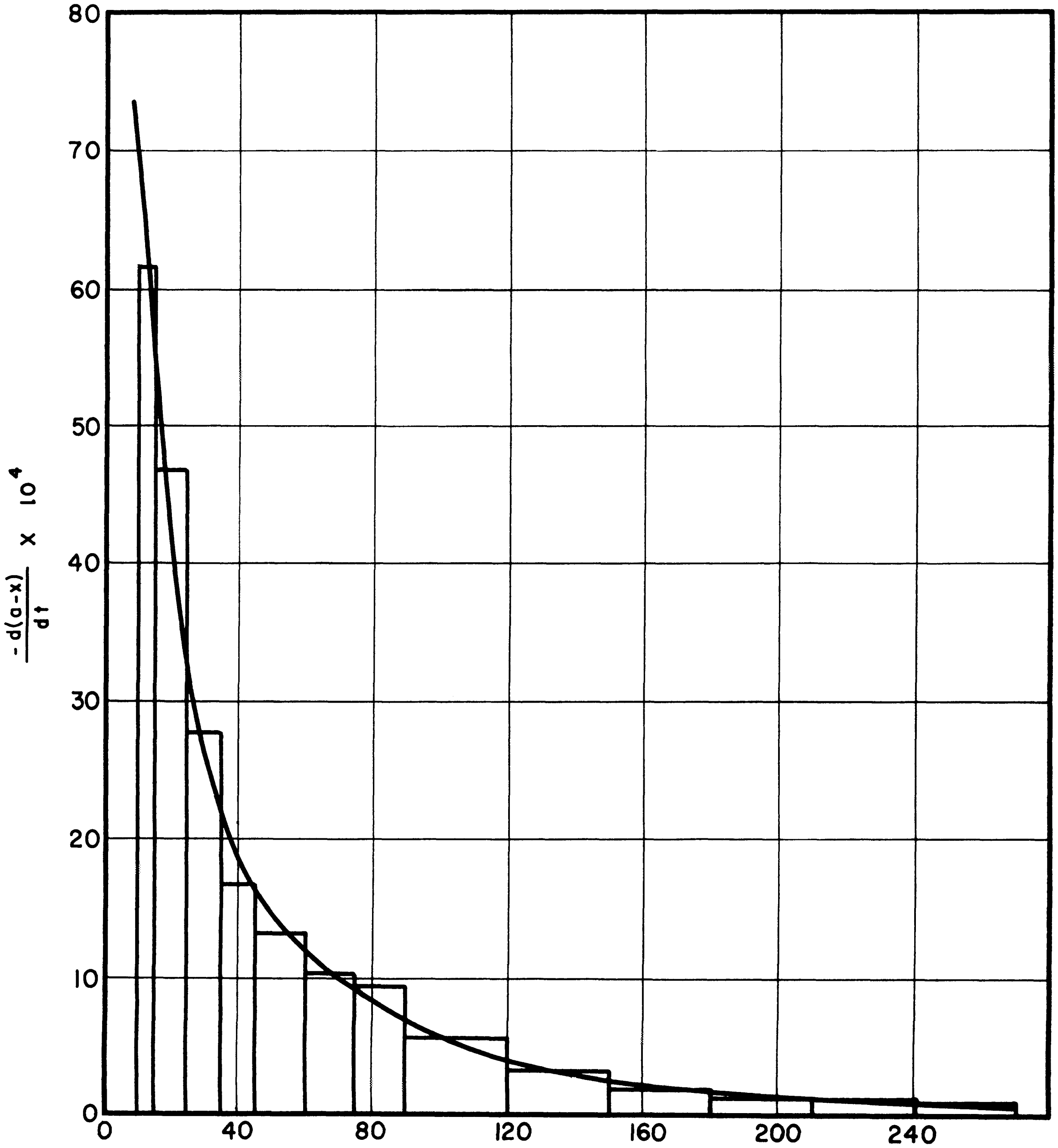
3. Set up two simultaneous equations involving the ratios of the rates of each other:

$$\frac{\left(-\frac{d(a-x)}{dt}\right)_1}{\left(-\frac{d(a-x)}{dt}\right)_2} = \frac{k_o(a-x)_1^{\alpha}\,(b-x)_1^{\beta}}{k_o(a-x)_2^{\alpha}\,(b-x)_2^{\beta}}$$

and

Figure 7

Smoothing Curve for Reaction Between
Oleic Acid and Glycerol at 218°C Using 50% Excess Glycerol



$$\frac{\left(-\frac{d(a-x)}{dt}\right)_3}{\left(-\frac{d(a-x)}{dt}\right)_4} = \frac{k_o(a-x)_3^{\alpha}\,(b-x)_3^{\beta}}{k_o(a-x)_4^{\alpha}\,(b-x)_4^{\beta}}$$

Taking logarithms yields

$$\log\frac{(\mathrm{Rate})_1}{(\mathrm{Rate})_2} = \alpha\log\frac{(a-x)_1}{(a-x)_2} + \beta\log\frac{(b-x)_1}{(b-x)_2}$$

and

$$\log\frac{(\mathrm{Rate})_3}{(\mathrm{Rate})_4} = \alpha\log\frac{(a-x)_3}{(a-x)_4} + \beta\log\frac{(b-x)_3}{(b-x)_4}$$

4. These two equations can now be easily solved for α and β. The solution for α and β is of the following form:

$$\alpha = \frac{A_1B_2 - A_2B_1}{C_1B_2 - C_2B_1}$$

and

$$\beta = \frac{A_3C_1 - A_1C_3}{B_2C_1 - B_1C_3}$$

where

$$A_1 = \log\frac{(\mathrm{Rate})_1}{(\mathrm{Rate})_2} \quad ; \quad A_2 = \log\frac{(\mathrm{Rate})_1}{(\mathrm{Rate})_4}$$

$$B_1 = \log\frac{(b-x)_1}{(b-x)_2} \quad ; \quad B_2 = \log\frac{(b-x)_3}{(b-x)_4}$$

$$C_1 = \log\frac{(a-x)_1}{(a-x)_2} \quad ; \quad C_2 = \log\frac{(a-x)_3}{(a-x)_4}$$

Thus, it is possible to set up numerous sets of equations and solve for α and β many times. This was done using the data obtained from the four reactions studied at 218°C and 199°C between oleic acid and glycerol. The value of α obtained fluctuated between 1.0 and 1.5 while the value of β obtained varied between 1.5 and 1.0. That is, when

$$\alpha = 1.0; \ \beta = 1.5$$

and when

$$\alpha = 1.5; \ \beta = 1.0$$

and furthermore when

$$\alpha = 1.2; \ \beta = 1.2$$

Therefore, it was assumed that

$$\alpha = \beta$$

and that the rate equation could be written thus:

$$-\frac{d(a-x)}{dt} = k_o\Big[(a-x)(b-x)\Big]^{\alpha} \qquad (3)$$

Notice that Equation 3 is the same as Equation 1 except for the exponent. This may indicate that the wrong order of reaction was assumed by earlier investigators.

If logarithms are taken on each side of Eq. (3) the following equation is obtained:

$$\log\left[-\frac{d(a-x)}{dt}\right] = \log k_o + \alpha \log\Big[(a-x)(b-x)\Big]$$

This equation is of the form

$$y = b + mx \ ,$$

and thus represents a straight line with a slope of α and an intercept of

$\log k_o$. That is, if $\log\left[-\frac{d(a-x)}{dt}\right]$ is plotted against $\log\left[(a-x)(b-x)\right]$ a straight line with a slope equal to α and an intercept equal to $\log k_o$ should be obtained.

Figure 8 represents a plot of $\log\left[-\frac{d(a-x)}{dt}\right]$ against $\log\left[(a-x)(b-x)\right]$ for the two reactions between oleic acid and glycerol at 199°C and Figure 9 is a similar plot for the two reactions at 218°C between the same compounds. In each case a straight line relationship is seen to exist. The slopes of the lines are between 1.17 and 1.20. However, the intercept, $\log k_o$, is apparently dependent upon both the temperature and the initial concentration. Just what was the dependence upon initial concentration was not immediately discernable.

The slope values, α, and the intercept values, k_o, (obtained from the $\log k_o$ which is the true intercept value), as determined by the method of least squares are given in Table 2 . A detailed explanation of the least squares method as used in these correlations appears in Appendix D.

Table 2

Rate Constants and Exponential Constants
for Four Reactions Between Oleic Acid and Glycerol Having
Various Initial Concentrations and Temperatures

Temp. °C	a $\frac{\text{eq. Acid}}{100\text{ gm}}$	b $\frac{\text{eq. OH}}{100\text{ gm}}$	$\frac{a}{b}$	$\frac{1}{b}$	k_o rate constant	α
199	.3040	.4606	.6600	2.1711	.0795	1.20
199	.3179	.3323	.9567	3.0093	.1154	1.20
218	.3045	.4561	.6676	2.1925	.1384	1.17
218	.3170	.3404	.9313	2.9377	.2066	1.18

Looking at Table 2 it is readily apparent that the rate constant, k_o, is dependent upon the ratios $\frac{a}{b}$ and $\frac{1}{b}$. That is:

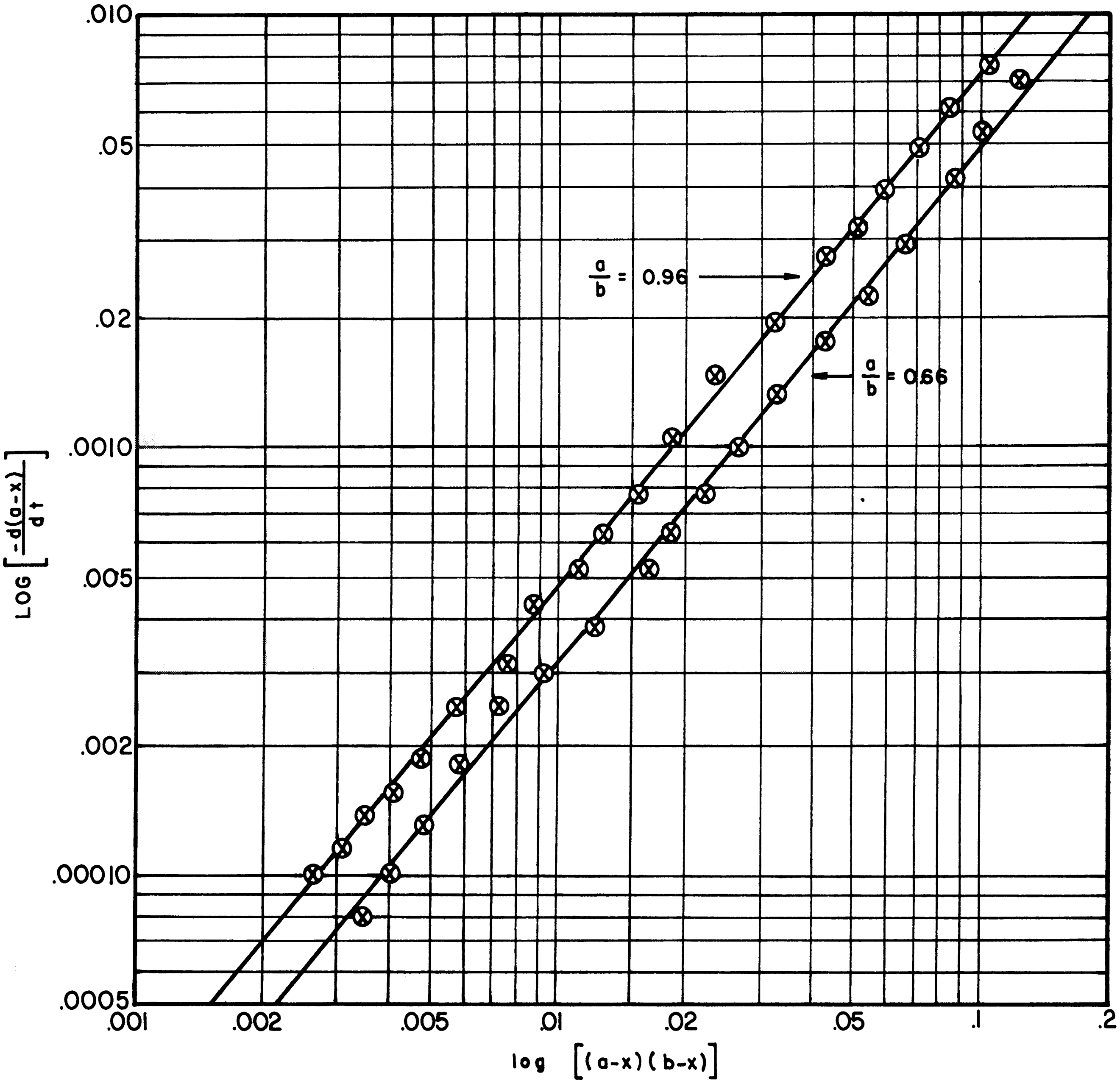


FIGURE 8

PLOT OF LOG $\left[\frac{-d(a-x)}{dt}\right]$ AGAINST

LOG [(a-x)(b-x)] FOR THE REACTION

BETWEEN OLEIC ACID AND GLYCEROL AT 199° C

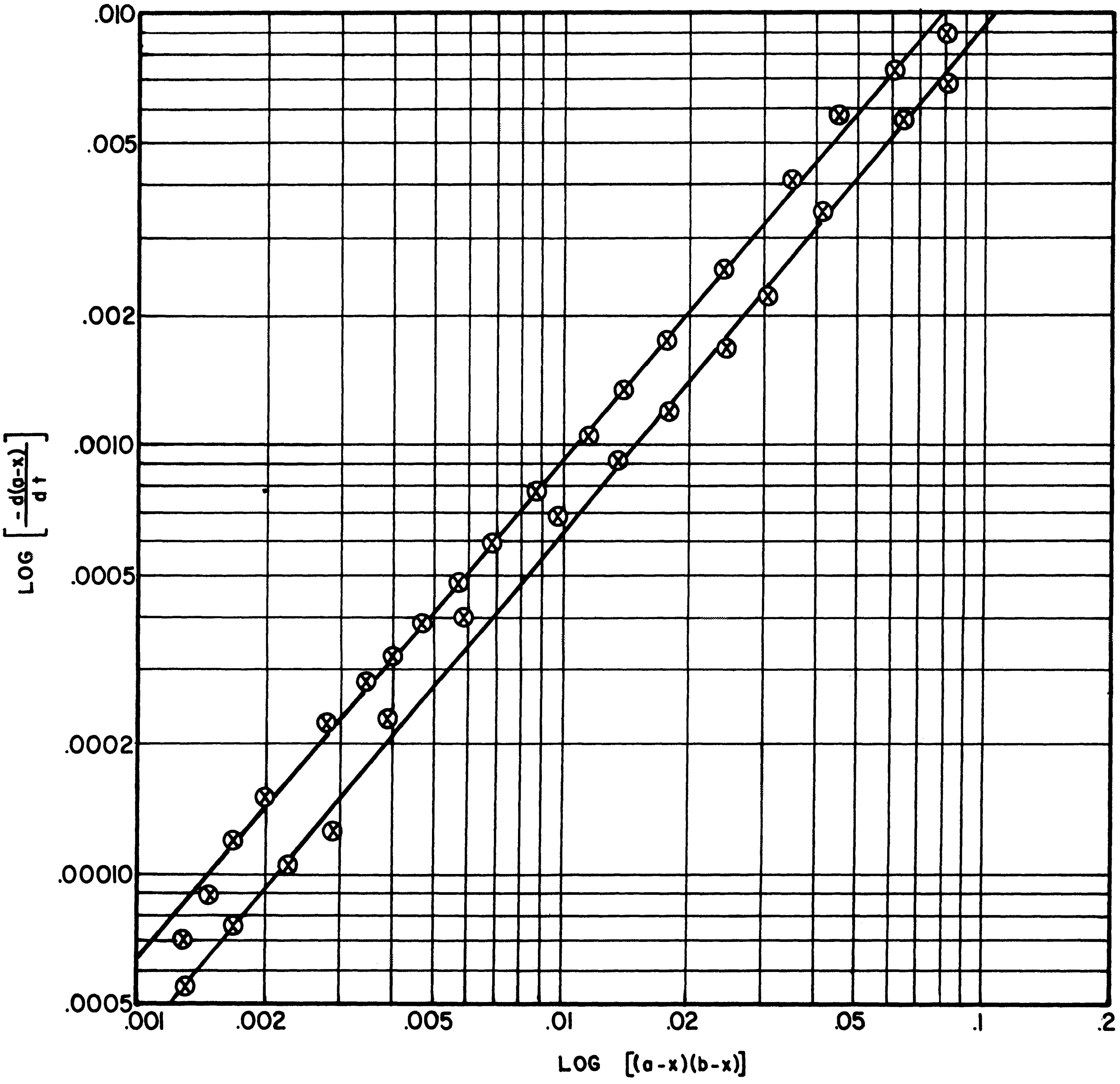


Figure 9

Plot of $\log\left[-\frac{d(a-x)}{dt}\right]$ Against $\log\left[(a-x)(b-x)\right]$

for Reaction Between Oleic Acid and Glycerol at 218° C

$$k_o = f(\tfrac{a}{b})$$

or

$$k_o = g(\tfrac{1}{b})$$

Since only two values of $\frac{1}{b}$ or $\frac{a}{b}$ were available it was not possible to plot k_o against these ratios to see if a straight line relationship existed. However, by comparing the ratios $\frac{(k_o)_S}{(k_o)_L}$, $\frac{(\frac{a}{b})_S}{(\frac{a}{b})_L}$, $\frac{(\frac{1}{b})_S}{(\frac{1}{b})_L}$, (subscript L means reaction where 50% equivalent excess of glycerol was used, while subscript S indicates reaction where a small, 4 or 7%, equivalent excess of glycerol was used) for each temperature, it was discovered that these ratios were nearly equal. Furthermore, if the $\frac{(\frac{1}{b})_S^{\alpha}}{(\frac{1}{b})_L}$ or $\frac{(\frac{a}{b})_S^{\alpha}}{(\frac{a}{b})_L}$ were used a better relationship was obtained part of the time. Table 3 gives the values of these ratios for the reactions run at 199°C and 218°C between oleic acid and glycerol.

Table 3

Comparison of $\frac{(k_o)_S}{(k_o)_L}$, $\frac{(\frac{a}{b})_S}{(\frac{a}{b})_L}$, $\frac{(\frac{1}{b})_S}{(\frac{1}{b})_L}$ Ratios

for Reactions Between Oleic Acid and Glycerol

Temp. °C	$\frac{(k_o)_S}{(k_o)_L}$	$\frac{(\frac{a}{b})_S}{(\frac{a}{b})_L}$	$\frac{(\frac{1}{b})_S}{(\frac{1}{b})_L}$	$\left[\frac{(\frac{a}{b})_S}{(\frac{a}{b})_L}\right]^{1.2}$	$\left[\frac{(\frac{1}{b})_S}{(\frac{1}{b})_L}\right]^{1.2}$
199	1.4516	1.4495	1.3861	1.5612	1.4796
218	1.4928	1.3950	1.3399	1.4910	1.4206

From Table 3 it is evident that any one of four different rate equations may be valid for the reaction of oleic acid with glycerol.

These equations are:

$$-\frac{d(a-x)}{dt} = k_1\left(\frac{1}{b}\right)\Big((a-x)(b-x)\Big)^{\alpha} \tag{4}$$

$$-\frac{d(a-x)}{dt} = k_2\left(\frac{a}{b}\right)\Big((a-x)(b-x)\Big)^{\alpha} \tag{5}$$

$$-\frac{d(a-x)}{dt} = k_3\left(\frac{1}{b}\;(a-x)(b-x)\right)^{\alpha} \tag{6}$$

$$-\frac{d(a-x)}{dt} = k_4\left(\frac{a}{b}\;(a-x)(b-x)\right)^{\alpha} \tag{7}$$

Due to the small amount of pure fatty acids available (1500 g stearic acid, 1200 g oleic acid, and 1000 g 95% linoleic acid), it was decided to try and determine which of the above equations (4,5,6 and 7) was most valid for the entire range of temperatures to be investigated (190 to 240°C) and for all three of the fatty acids reacted with glycerol by the following procedure:

1. Vary the excess amount of glycerol used between 0 and 50%. Use a slight excess of acid (less than 10%) at least once.
2. Vary the temperature between 190 and 240°C at the same time the excess glycerol is being varied. Use at least four different temperatures for each acid.
3. Plot $\log\left[-\frac{d(a-x)}{dt}\right]$ against $\log\left[(a-x)(b-x)\right]$ and determine the slope, α, and the intercept, log k, if a straight line is obtained.
4. Determine the rate constants for each of the four equations listed above (equations 4,5,6 and 7).

5. Plot the $\log k_1$, $\log k_2$, $\log k_3$ and $\log k_4$ values against $\frac{1}{T}$ to see if the Arrhenius equation applies. The Arrhenius equation is

$$k = Ae^{-E_o/RT}$$

where A is a constant, commonly called the frequency factor, E_o is the Activation Energy, R is the Universal Gas Constant, and T is the absolute temperature in °K. Taking logarithms of both sides yields:

$$\log k = \log A \frac{E_o}{2.303\ RT}$$

Thus a plot of log k against $\frac{1}{T}$ should be a straight line with a slope of $\frac{E_o}{2.303\ RT}$ and an intercept of log A. In this case it was presupposed that the Arrhenius plot having the best straight lines would show that the k used in that plot came from the most valid rate equation.

It was recognized at this point that perhaps different results would be obtained for each acid and/or that perhaps all four of the rate equations would be shown to be invalid. However, in view of the data obtained on the reaction of oleic acid with glycerol it was felt that the procedure outlined above would produce results which could be used to predict accurately the results of any glycerol-fatty acid esterification reaction run inside the operating range of this data.

Tabulated in Table 4 are the operating conditions used for each of the reactions between glycerol and either stearic, oleic or linoleic acid. Also included in Table 4 are the reaction rate constants obtained

Table 4

Operating Conditions, Exponential Constants and Rate Constants for the Esterifications of Glycerol with Stearic, Oleic and Linoleic Acid

Temp. ± 1°C	$\frac{a}{b}$	$\frac{1}{b}$	α	Rate Constants			
				k_1 (1)	k_2 (2)	k_3 (3)	k_4 (4)
Stearic Acid							
190	1.0000	3.1516	1.23	0.0268	0.0844	0.0205	0.0844
191	.6769	2.2326	1.17	.0256	.0843	.0225	.0898
204	.6477	2.1496	1.16	.0358	.1189	.0316	.1276
222	1.0000	3.1516	1.19	.0657	.2070	.0530	.2070
223	1.0000	3.1516	1.23	.0704	.2219	.0535	.2219
227	.6640	2.1959	1.16	.0706	.2334	.0623	.2484
244	.6515	2.1603	1.15	.1209	.4007	.1073	.4281
Oleic Acid							
199	.6600	2.1711	1.20	.0366	.1205	.0313	.1342
199	.9567	3.0093	1.20	.0384	.1206	.0307	.1210
218	.6676	2.1925	1.17	.0631	.2073	.0551	.2222
218	.9313	2.9377	1.18	.0703	.2219	.0592	.2247
234	.9631	3.0276	1.20	.1125	.3536	.0900	.3535
240	.6413	2.1186	1.19	.1261	.4167	.1128	.4649
Linoleic Acid							
187	.6618	2.1626	1.20	.0282	.0923	.0243	.1000
198	1.0000	3.1114	1.15	.0391	.1219	.0330	.1219
202	1.0691	3.3047	1.16	.0458	.1416	.0386	.1475
208	1.0000	3.1114	1.12	.0499	.1553	.0439	.1553
228	.7332	2.3629	1.18	.1044	.3364	.0891	.3564

$$(1) \quad -\frac{d(a-x)}{dt} = k_1\left(\frac{1}{b}\right)\Big((a-x)(b-x)\Big)^{\alpha} \qquad \text{Eq. 4}$$

$$(2) \quad -\frac{d(a-x)}{dt} = k_2\left(\frac{a}{b}\right)\Big((a-x)(b-x)\Big)^{\alpha} \qquad \text{Eq. 5}$$

$$(3) \quad -\frac{d(a-x)}{dt} = k_3\left(\frac{1}{b}\,(a-x)(b-x)\right)^{\alpha} \qquad \text{Eq. 6}$$

$$(4) \quad -\frac{d(a-x)}{dt} = k_4\left(\frac{a}{b}\,(a-x)(b-x)\right)^{\alpha} \qquad \text{Eq. 7}$$

from each of the four postulated rate equations (equations 4,5,6 and 7).

Figures 10, 11, 12 and 13 are Arrhenius plots of log k_1, $\log_2$, log k_3 and log k_4 respectively, against the reciprocal of the absolute temperature, 1/T. From these plots it is evident that there is not much difference between the reactivity of the three fatty acids studied. However, these plots do show that although the reactivity differences are small, the more unsaturated acids esterify with glycerol faster than the more saturated acids. It is also evident from these plots that all four of the rate constants from the four postulated rate equations obey (within experimental error) the Arrhenius Equation:

$$k = Ae^{-E_0/RT} \quad .$$

Thus the experimental procedure followed up to this time was not sufficient to distinguish which of the four postulated rate equations is the true rate equation that should be used for these reactions. Therefore, a different experimental technique was necessary to determine which of the four rate equations was the proper one to use to predict reaction rates in the future. Before a new experimental technique was tried the following was done:

1. The Activation Energies and "Collision Factors" were calculated from the Arrhenius plots and compared with values previously reported for similar esterifications.
2. It was determined if the data of Feuge, Kraemer and Bailey (17) could be correlated in the manner which has been introduced by the writer.

Figure 10

Log k_1 as a Function of $\frac{1}{T}$ for Reactions
Between Stearic, Oleic and Linoleic Acids and Glycerol

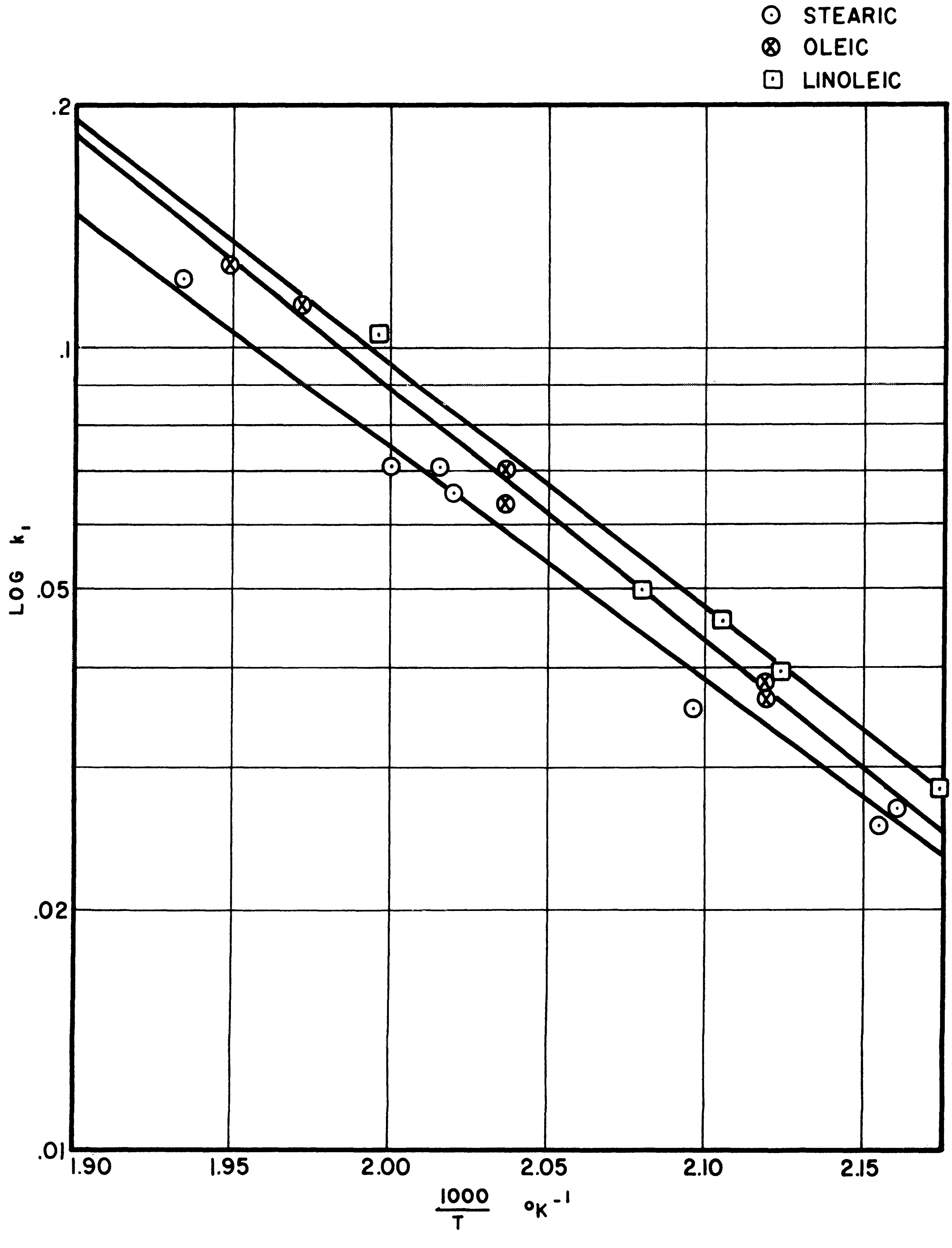


Figure 11

Log k_2 as a Function of $\frac{1}{T}$ for Reactions Between Stearic, Oleic and Linoleic Acids and Glycerol

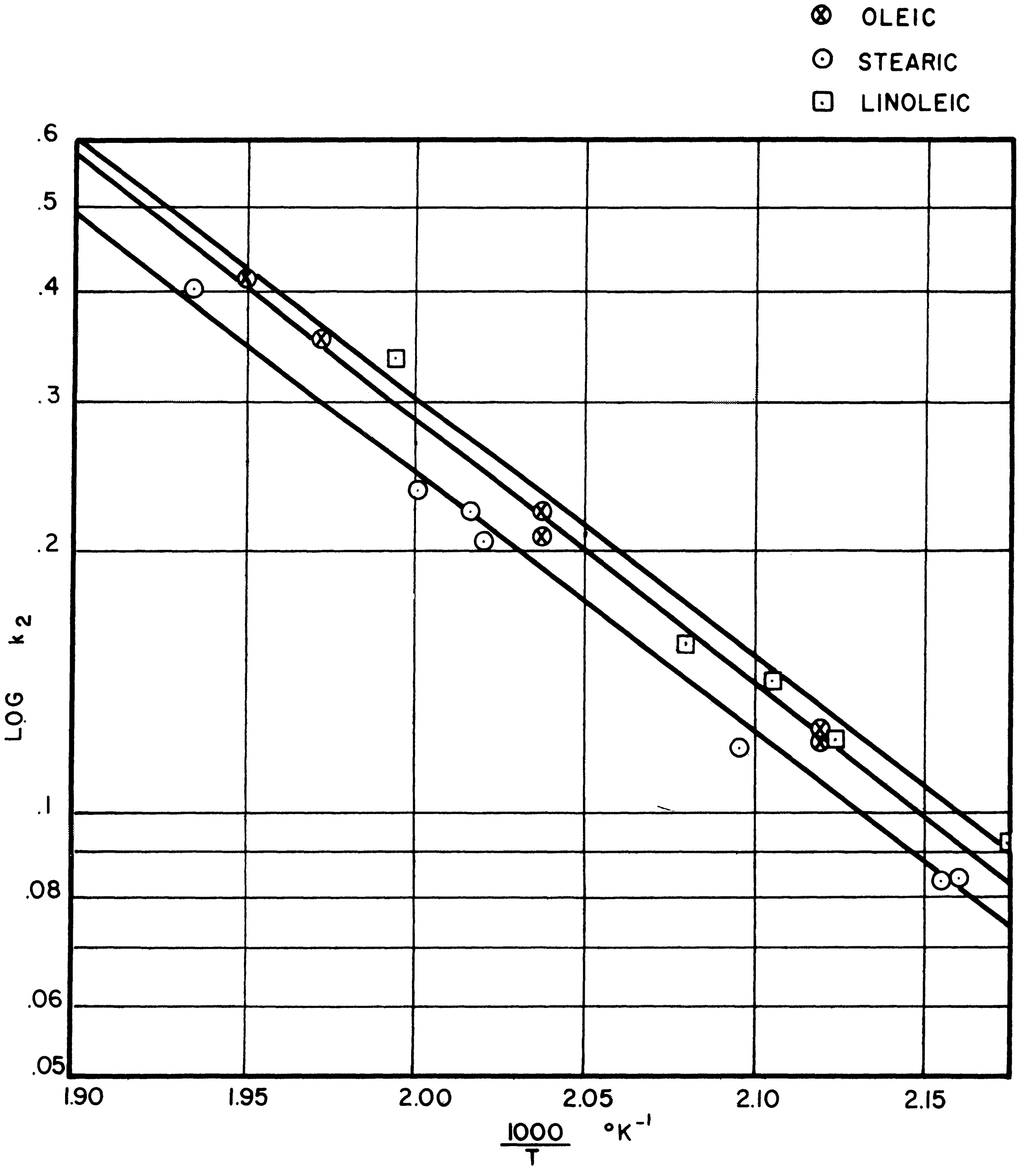
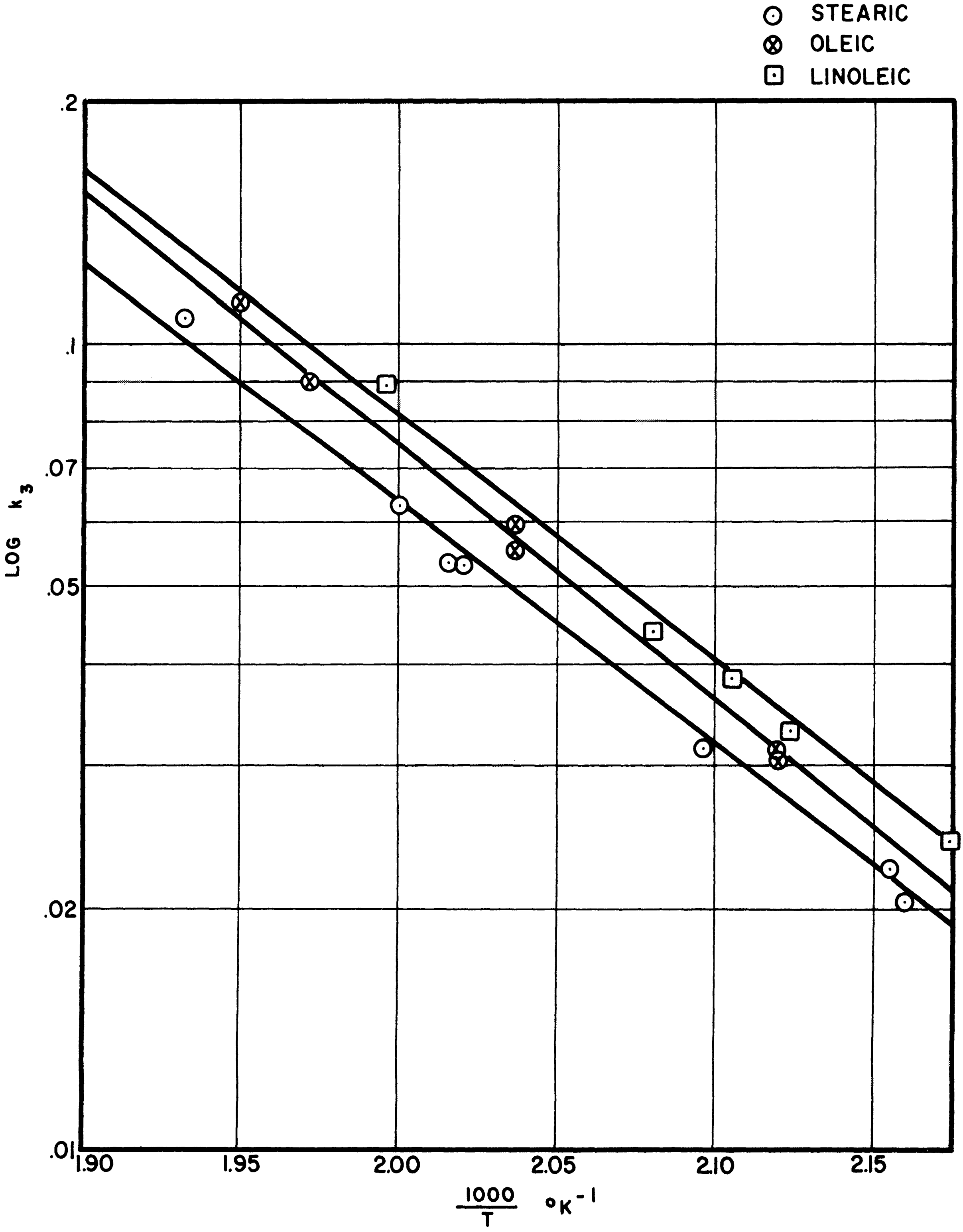


Figure 12

Log k_3 as a Function of $\frac{1}{T}$ for Reactions Between Stearic, Oleic and Linoleic Acids and Glycerol



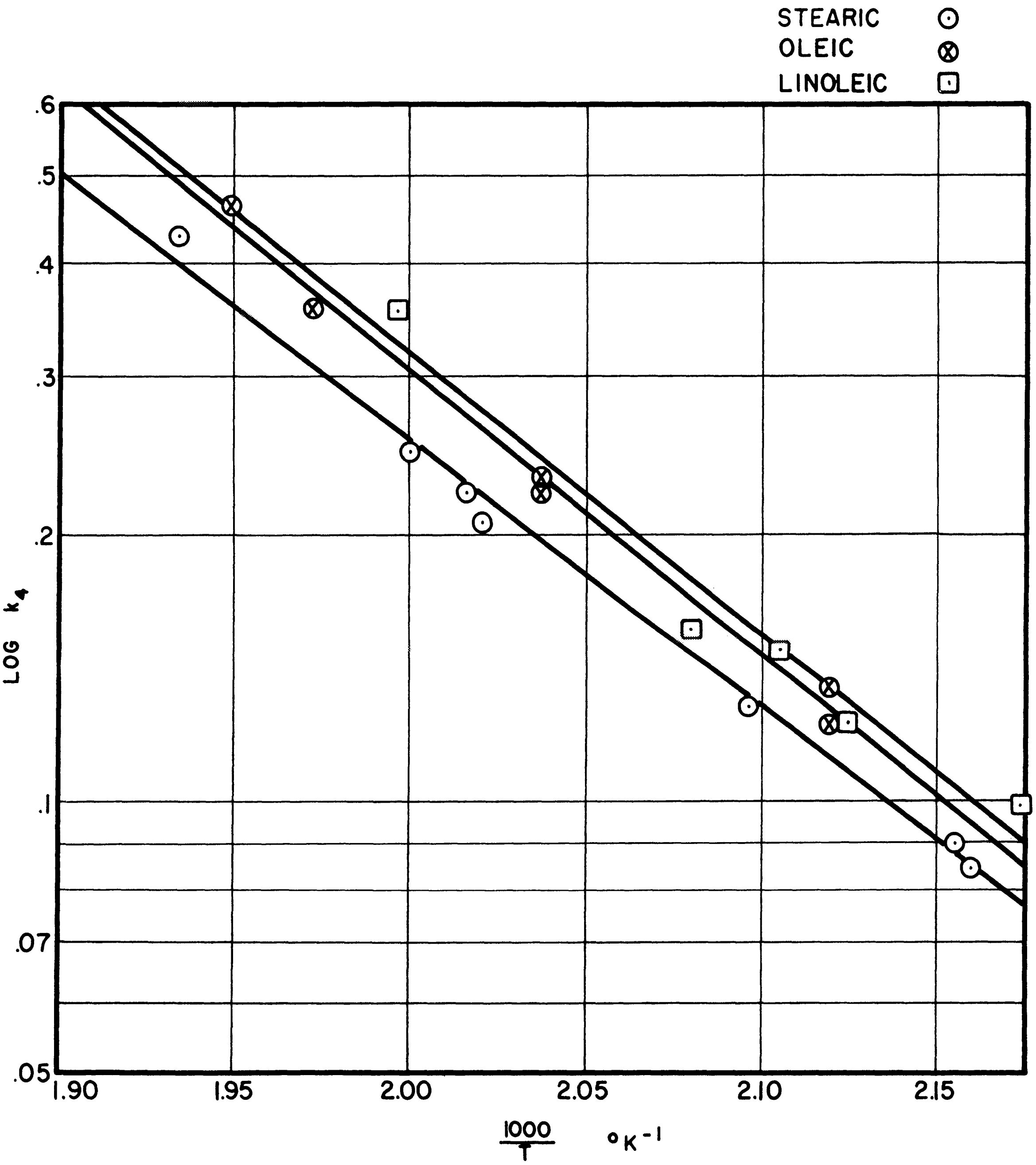


Figure 13

Log k_4 as a Function of $\frac{1}{T}$ for Reactions Between Stearic, Oleic and Linoleic Acids and Glycerol

The Activation Energies, E_o, and the "Collision Factors", A, were calculated for each acid for each of four postulated rate expressions, using the method of least squares to evaluate the slopes and intercepts. The values of these constants are listed in Table 5.

These values compare very favorably with the values obtained by other investigators. The Activation Energies are a little higher than those reported by Feuge, Kraemer and Bailey (17), but are still in the 10,000 to 15,000 cal/mole range found to be correct for fatty acid esterifications by Hinshelwood et.al. (16,25,26). The Activation Energies calculated from the Northwestern Production Club paper (36) also agree very well with the above values calculated for the pure fatty acids.

It is interesting to note that the Activation Energy of oleic acid is apparently greater than the Activation Energy of both stearic and linoleic acid. However, the Activation Energy of linoleic acid is higher than the Activation Energy of stearic acid.

Oleic acid also has the largest "Collision Factor" values, with linoleic acid having the next largest values and stearic acid the lowest values. However, due to its greater Activation Energy (slope of straight line in log k vs 1/T plot) oleic acid has lower rate constant values than linoleic acid in the range of temperatures investigated.

The next step was to correlate the published data of Feuge, Kraemer and Bailey (17) in the same manner as the present data. This was done and in Figure 14 $\log\left[-\frac{d(a-x)}{dt}\right]$ against $\log (a-x)^2$ for each temperature is plotted. Notice that $\log (a-x)^2$ is used since Feuge, Kraemer and Bailey (17) used equivalent ($a = b$ or $\frac{a}{b} = 1$) amounts of acid and glycerol during their investigation.

Table 5

Activation Energies and "Collision Factors" for the Reactions Between Stearic, Oleic and Linoleic Acid and Glycerol Using the Rate Constants from Equations 4,5,6 and 7.

Acid	k_1 from Eq. 4 E_o cal/mole	 A	k_2 from Eq. 5 E_o cal/mole	 A	k_3 from Eq. 6 E_o cal/mole	 A	k_4 from Eq. 7 E_o cal/mole	 A
Stearic	13,500	5.95×10^4	13,600	2.17×10^5	13,900	7.50×10^4	13,700	2.52×10^5
Oleic	14,800	2.49×10^5	14,700	7.79×10^5	15,100	2.96×10^5	14,800	8.99×10^5
Linoleic	14,200	1.62×10^5	14,200	4.98×10^5	14,200	1.29×10^5	14,100	4.65×10^5

This data produced straight lines, exactly as the present data, when plotted this way. The slopes of these lines were in the same range as the slopes of the lines previously obtained, 1.12 to 1.23. Just as a matter of interest, the reaction rate constants were calculated for this data according to equations 4,5,6 and 7. Of course the constants were the same for equations 5 and 7 since equivalent amounts of acid and glycerol were used (making $\frac{a}{b} = 1.0$). Listed in Table 6 are the values of these rate constants as well as the slopes of the lines, α. In addition an Arrhenius plot was made of the rate constants and this is represented by Figure 15. The Activation Energy and "Collision Factors" were calculated for each of the rate constants and these are given in Table 7 .

If the rate constants for Feuge, Kraemer and Bailey's (17) data are compared with the rate constants for the writer's data it is seen that the writer's rate constants have considerably lower values. This can be attributed to differences in operating conditions between the two sets of data. It is likely that Feuge, Kraemer and Bailey (17) used a higher rate of agitation in addition to the lower pressure (20 mm Hg to atmospheric pressure) already mentioned. Also a higher inert gas flow could conceivably cause higher rate constants. The important thing, however, is the fact that the author s correlation can be used satisfactotily to correlate Feuge, Kraemer and Bailey s data.

It seems peculiar, however, that the Activation Energies should be so much higher for Feuge, Kraemer and Bailey's (17) data when their data is correlated by either equation 4,5,6 or 7. (see Table 7). These values are outside the range predicted by Hinshelwood and others (16,25,26).

Figure 14

Plot of log $-\frac{d(a-x)}{dt}$ Against log $(a-x)(b-x)$ from Data of Feuge, Kraemer and Bailey (17)

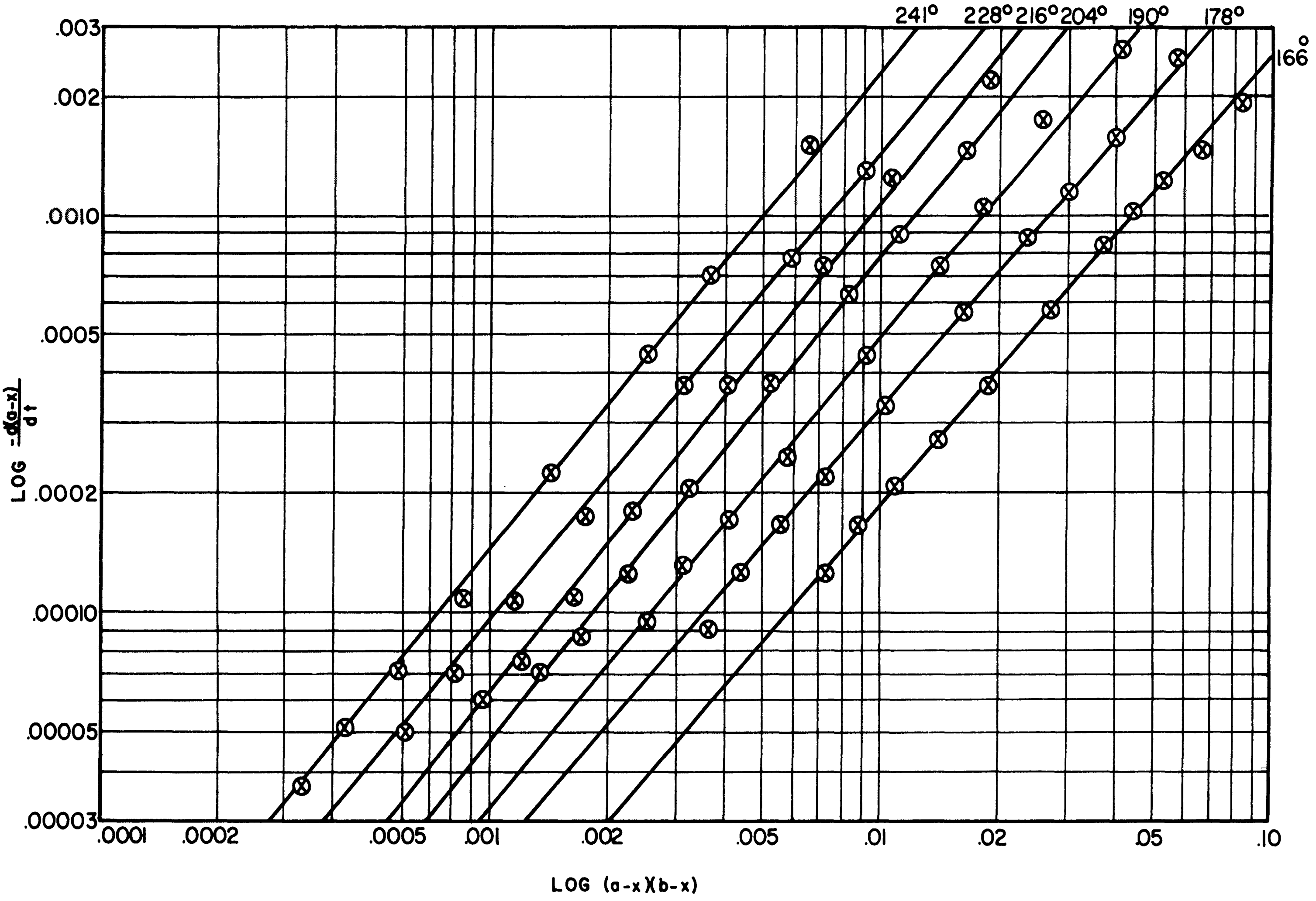


Table 6

Rate Constants for Data of Feuge, Kraemer and Bailey (17) When Correlated According to Equations 4, 5, 6 and 7.

Temp. °C	$\frac{a}{b}$	$\frac{1}{b}$	α	Rate Constants			
				k_1	k_2	k_3	k_4
166	1.00	3.1606	1.12	0.0102	0.0324	0.0089	0.0324
178	1.00	3.1606	1.17	.0216	.0683	.0179	.0683
190	1.00	3.1606	1.19	.0382	.1206	.0305	.1206
204	1.00	3.1606	1.22	.0705	.2229	.0545	.2229
216	1.00	3.1606	1.25	.1058	.3345	.0796	.3345
225	1.00	3.1606	1.22	.1234	.3900	.0956	.3900
241	1.00	3.1606	1.23	.2230	.7048	.1704	.7048

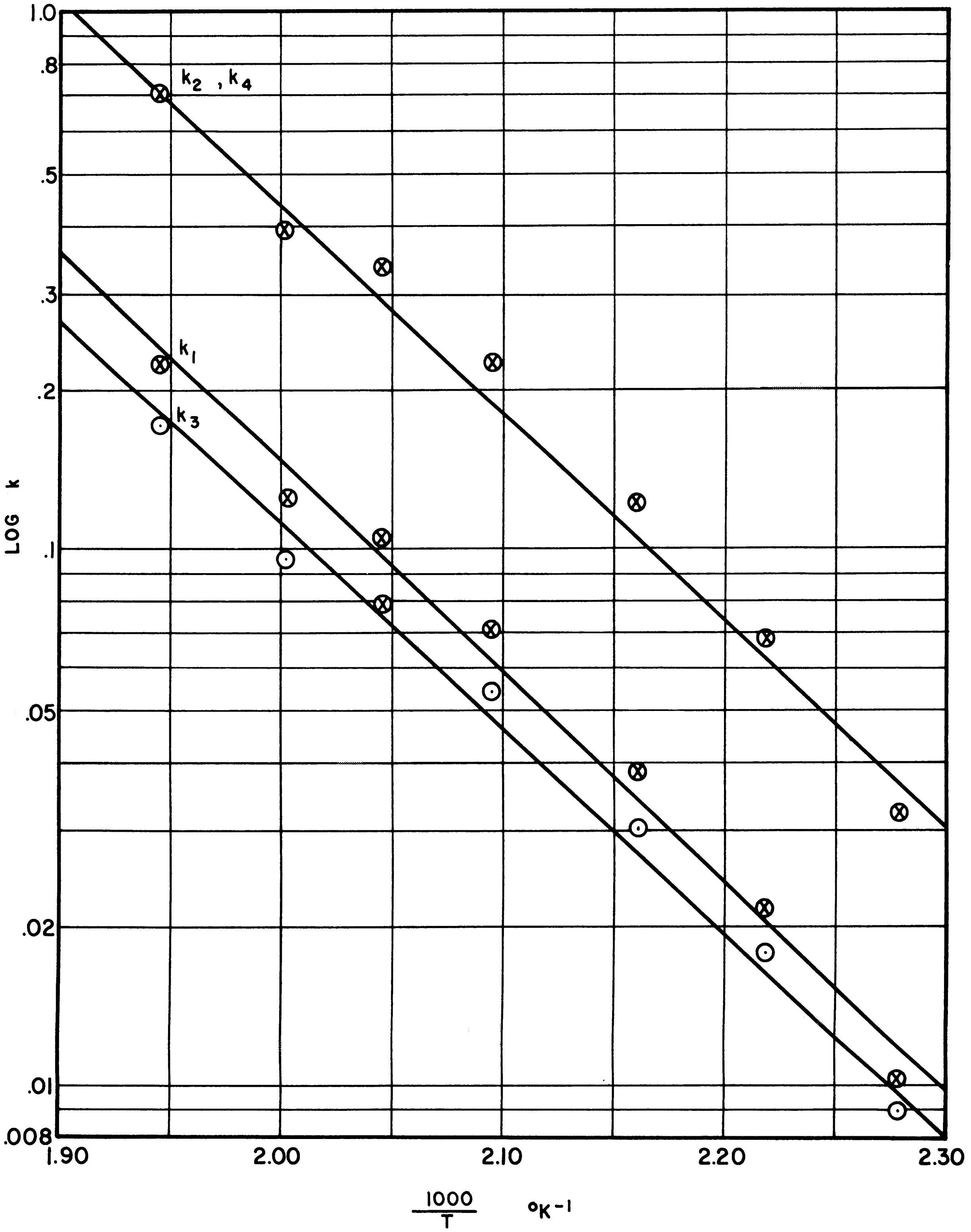
Table 7

Activation Energies and "Collision Factors" for the Reactions of Peanut Oil Fatty Acids and Glycerol Using Data of Feuge, Kraemer and Bailey, Correlated According to Equations 4, 5, 6 and 7.

Equation Number	E_o cal/mole	A
4	18,000	1.13×10^7
5	18,000	3.50×10^7
6	17,200	3.86×10^6
7	18,000	3.50×10^7

Figure 15

Plot of Log k Against $\frac{1}{T}$ Using
Data of Feuge, Kraemer and Bailey (17)
Correlated According to Equations 4, 5, 6 and 7.



Why this occurs is not the important factor. Instead, as mentioned before, the fact that Feuge et.al.'s data can be correlated according to equations 4,5,6 and 7 can be taken as proof that in the range of operating conditions being used one or all of these equations may be used to predict reaction rates.

The next step was to determine which of the four postulated equations, if any, was valid outside the range of operating conditions used up to the present time. It was felt that an extension of the temperature range was unnecessary, since that would only tend to increase the accuracy of the Activation Energy and "Collision Factor" calculations. Instead it was decided that the range of $\frac{a}{b}$ and $\frac{1}{b}$ values should be extended and several values of $\frac{a}{b}$ and $\frac{1}{b}$ should be studied at one temperature.

However, there was no more pure acid available for these reactions. Therefore, it was decided, in view of the fact that all three acids exhibited nearly the same reactivity, that an impure, but commercially pure grade of acid could be used. There was some Emersol 233 LL Elaine which had been used as a starting material for making pure oleic acid, immediately available, so it was used as a source of fatty acids. The composition of Emersol 233 LL Elaine is approximately 87% oleic acid, 4% linoleic acid and 9% saturated acids.

Two reactions between Emersol 233 LL Elaine and glycerol were studied at 205°C. These reactions were carried out by adding either acid or glycerol to the other component in steps as follows:

1. Glycerol was reacted with a large excess of acid (500%) until nearly all the glycerol had been reacted. This

could be approximated by measuring the water given off by the reaction. At this time more glycerol was added to the reaction mixture and allowed to react until used up. This was then repeated two more times, making a total of four glycerol additions or four steps to the reaction. During the final step there was nearly equivalent amounts of free acid and glycerol in the reaction mixture. This permitted the variation of the $\frac{a}{b}$ ratio between the limits of 5.07 and 1.03 and the $\frac{1}{b}$ ratio between 14.5 and 7.95.

2. Acid was reacted with a large excess (300%) of glycerol until nearly all the acid had been reacted (as determined by the amount of water of reaction that had been collected). Then more acid was added and allowed to react, etc. A total of four additions of acid were made. Once again during the final step, nearly equivalent amounts of acid and glycerol were present. A smaller excess of glycerol was used initially because a larger excess would have exceeded the miscibility limit of the acid in the glycerol. The $\frac{a}{b}$ ratio varied between 0.415 and 0.81 while the $\frac{1}{b}$ ratio varied between 1.51 and 11.4.

The data obtained from these two runs was correlated according to equation 3 which is:

$$-\frac{d(a-x)}{dt} = k_o\left[(a-x)(b-x)\right]^{\alpha} \qquad \text{Eq. 3}$$

This equation was used instead of equations 4,5,6 and 7 as before because the purpose of these two runs was to determine what relationship, if any, existed between the reaction rate constant, k_o, and the ratios $\frac{a}{b}$ and $\frac{1}{b}$.

Figures 16 and 17 are plots of the data obtained in these two runs. Both are plots of $\log\left[-\frac{d(a-x)}{dt}\right]$ against $\log\left[(a-x)(b-x)\right]$. Note that a different line is obtained for each step in each reaction. The slopes of these lines as well as the reaction rate constant for each step were calculated and are tabulated in Table 8.

Table 8

Reaction Rate Constants of Two Reactions Between
Emersol 233 LL Elaine and Glycerol Where Either the
Acid or Glycerol Was Added to the
Reaction Mixture in Four Steps

$\frac{a}{b}$	$\frac{1}{b}$	α	k_o	Step	
5.0651	14.4718	1.14	0.3335	1	Glycerol
3.3590	12.0482	1.22	.2964	2	Added
2.5835	12.8534	1.15	.3080	3	to
1.0191	7.9428	1.12	.2240	4	Acid
.8109	11.3895	1.16	.2705	4	Acid
.5055	6.1576	1.12	.1677	3	Added
.4065	3.3875	1.13	.1286	2	to
.4312	1.5129	1.11	.0789	1	Glycerol

Equations 4,5,6 and 7 assume that the reaction rate constant is related to the ratio $\frac{a}{b}$ or the ratio $\frac{1}{b}$ as follows:

Figure 16

$\text{Log}\left[-\frac{d(a-x)}{dt}\right]$ as a Function of $\text{Log}\left[(a-x)(b-x)\right]$

for Reaction Between Emersol 233 LL Elaine and Glycerol at 205°C Where Glycerol was Added to the Acid in 4 Steps.

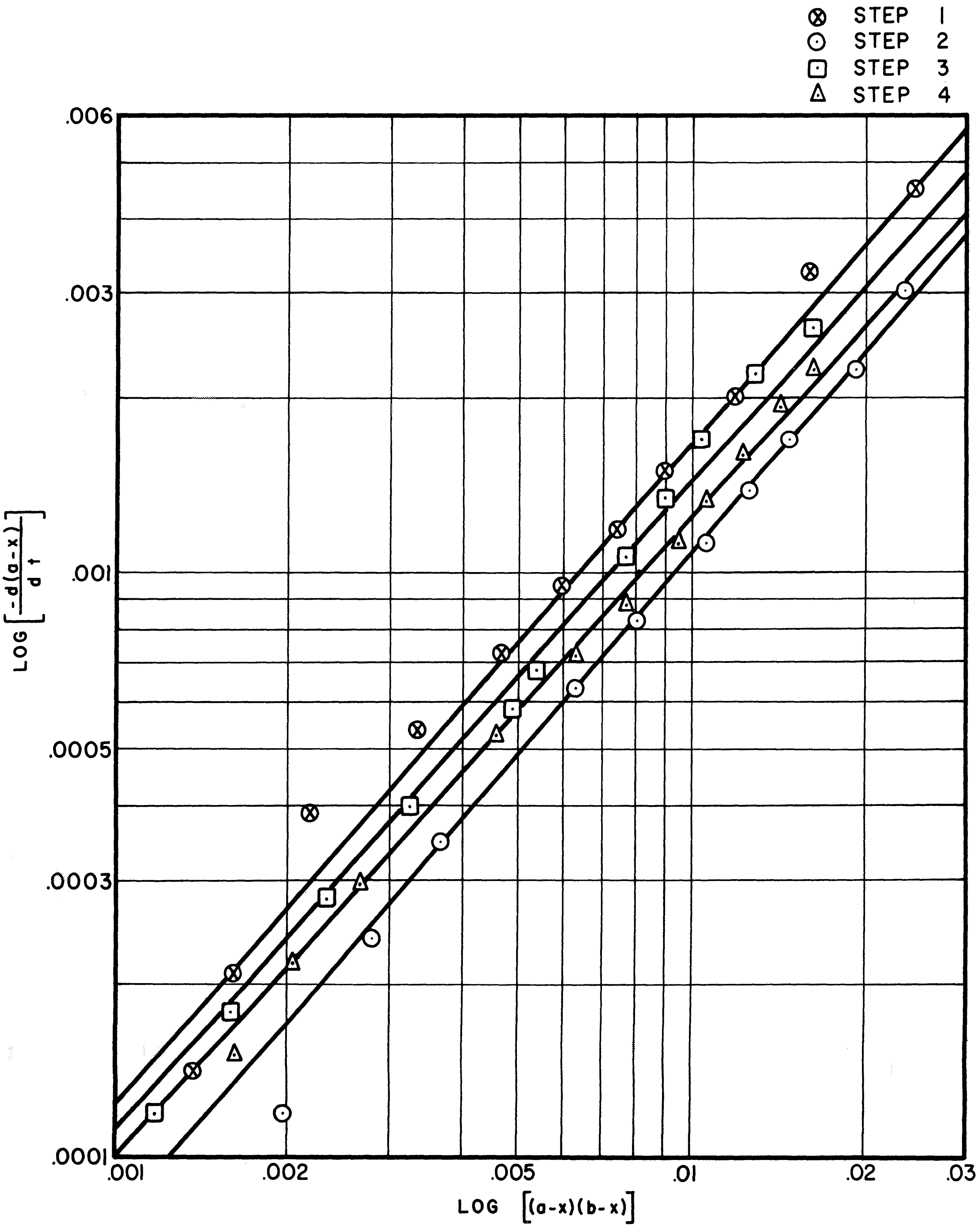
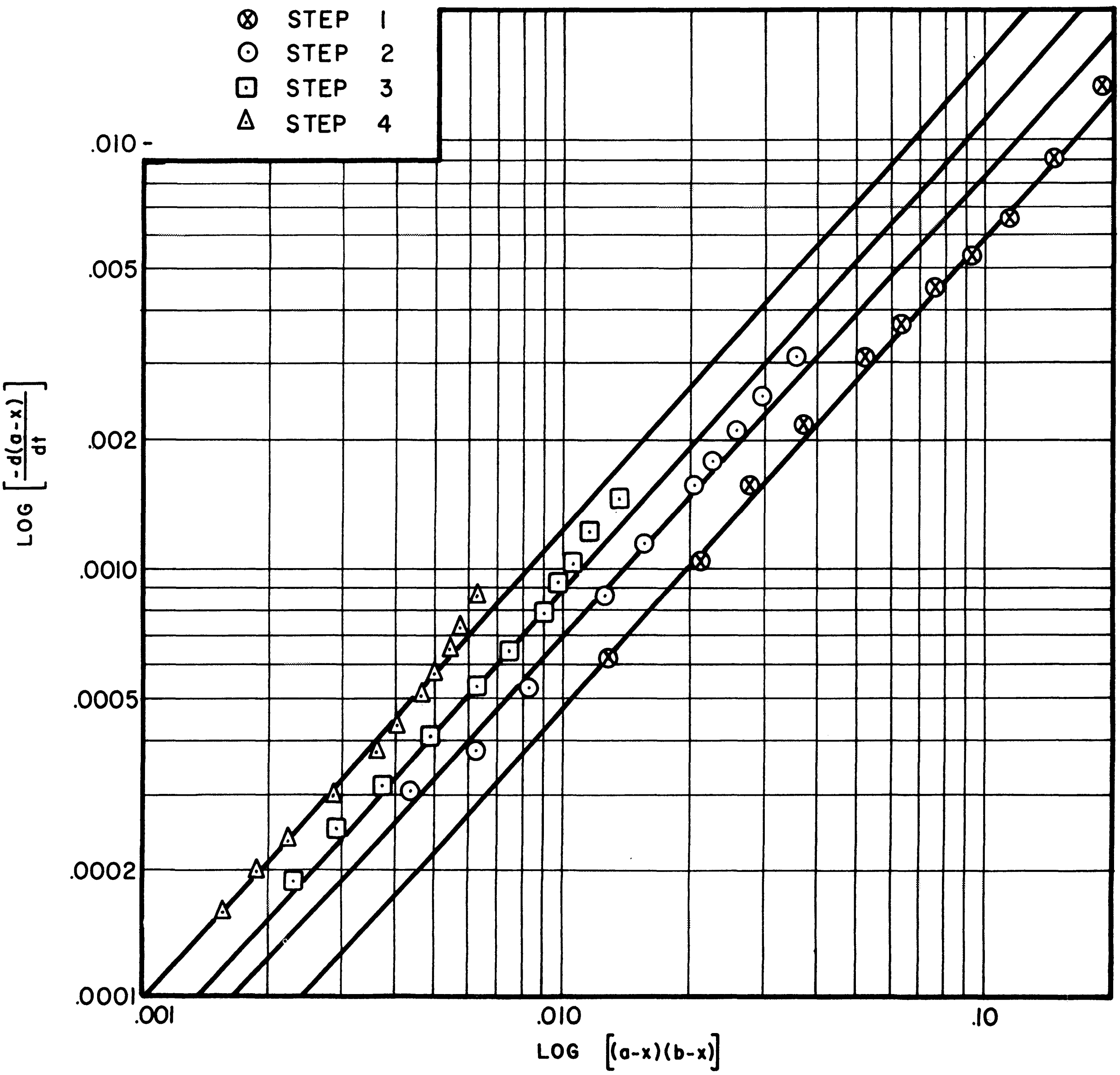


Figure 17

$\text{Log}\left[-\frac{d(a-x)}{dt}\right]$ as a Function of $\text{Log}\left[(a-x)(b-x)\right]$
for Reaction Between Emersol 233 LL Elaine
and Glycerol at 205°C Where Acid was Added to Glycerol in 4 Steps.



$k_o = k_1(\frac{1}{b})$ from equation 4

$k_o = k_2(\frac{a}{b})$ from equation 5

$k_o = k_3(\frac{1}{b})^{\alpha}$ from equation 6

$k_o = k_4(\frac{a}{b})^{\alpha}$ from equation 7

Therefore if a plot of k_o against $\frac{1}{b}$ yields a straight line, equation 4 is valid for the entire range of $\frac{1}{b}$ values. Similarly, equation 6 is valid over the range if a plot of log k_o against log $\frac{1}{b}$ is a straight line with a slope of α. Equation 5 is valid if a plot of k_o against $\frac{a}{b}$ yields a straight line and equation 7 is valid if log k_o plotted against log $\frac{a}{b}$ is a straight line with a slope of α. These four plots are represented by Figures 18, 19, 20 and 21.

Looking at Figures 20 and 21 it is evident that the reaction rate constant is not a simple function of the ratio $\frac{a}{b}$. In neither the plot of k_o against $\frac{a}{b}$ (Figure 20) nor the plot of log k_o against log $\frac{a}{b}$ (Figure 21) was a straight line relationship obtained. However, these plots do show that a linear relationship between k_o and the ratio $\frac{a}{b}$ could exist over a narrow range as was the case with the initial phase of this investigation.

In the case where k_o was plotted as a function of $\frac{1}{b}$ as well as where log k_o was plotted against log $\frac{1}{b}$ a straight line was obtained. This indicates that k_o is dependent upon the ratio $\frac{1}{b}$. This dependence can be expressed by the following equations

$$k_o = k' + \frac{k''}{b} \quad \text{from Figure 18} \qquad (8)$$

or

$$k_o = k\ (\frac{1}{b})^{\gamma} \quad \text{from Figure 19} \qquad (9)$$

Figure 18

Between k_o as a Function of $\frac{1}{b}$ for the Reactions Between Emersol 233 LL Elaine and Glycerol at 205°C Where Either the Acid or Glycerol was Added in Steps.

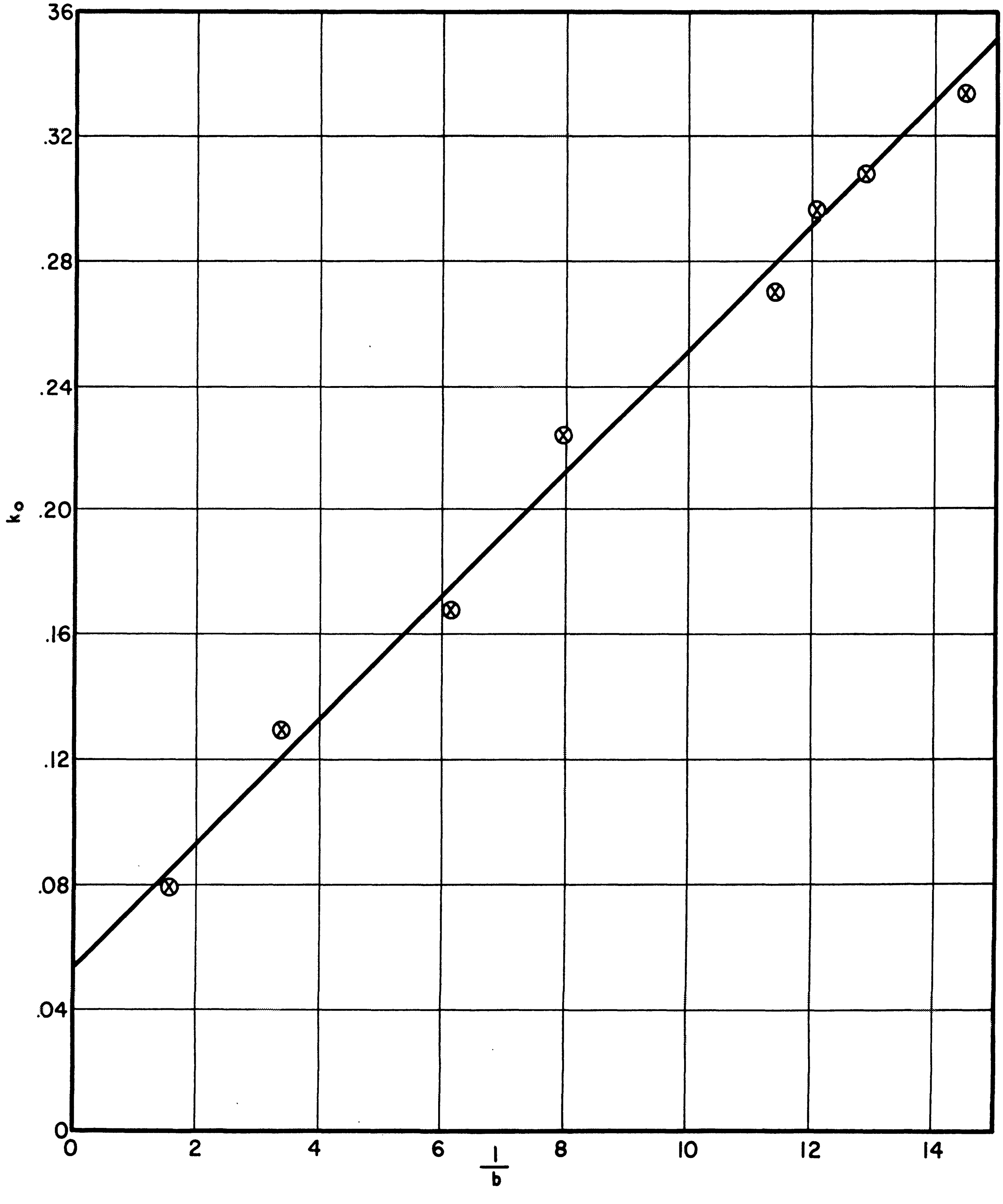


Figure 19

Log k_o as a Function of Log $\frac{1}{b}$ for Reactions Between Emersol 233 LL Elaine and Glycerol at 205°C Where Either the Acid or Glycerol was Added in Steps

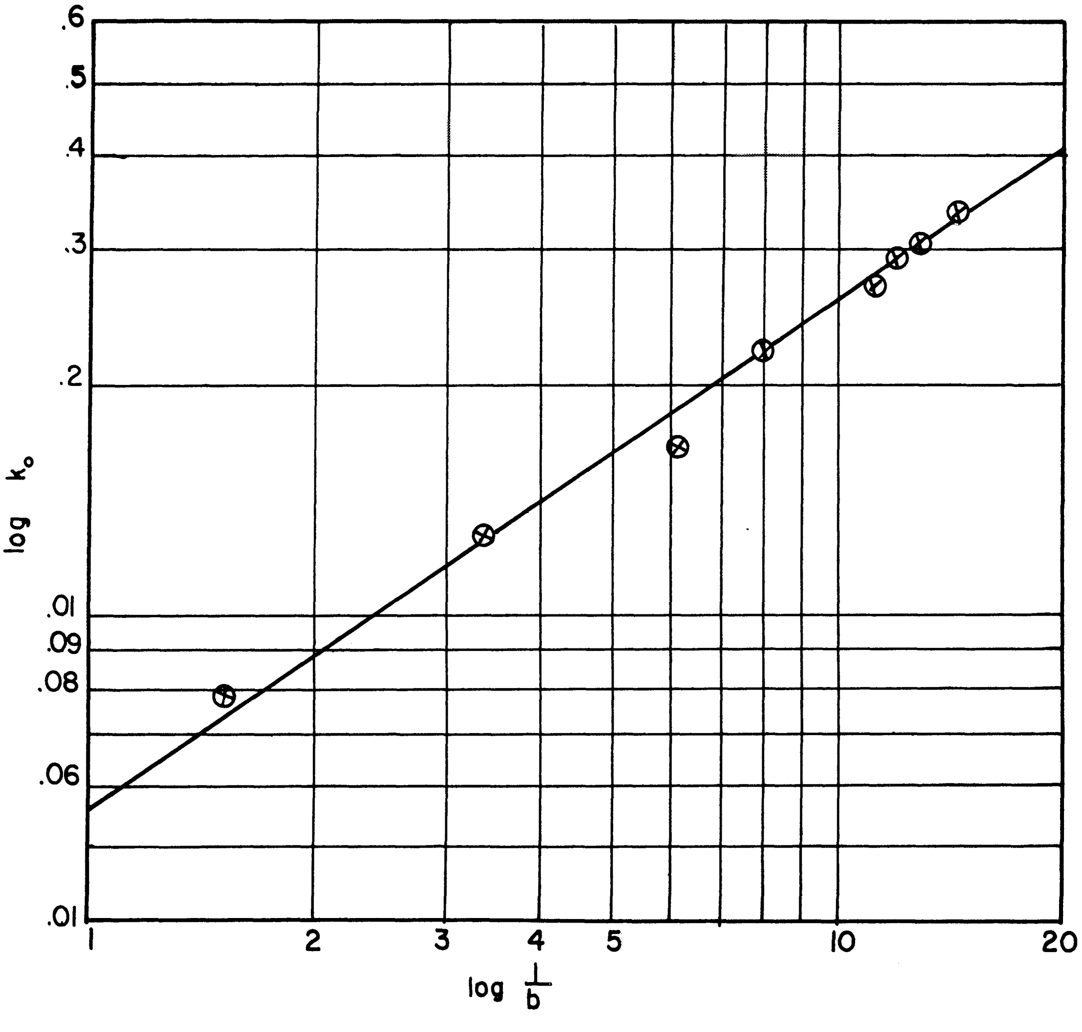
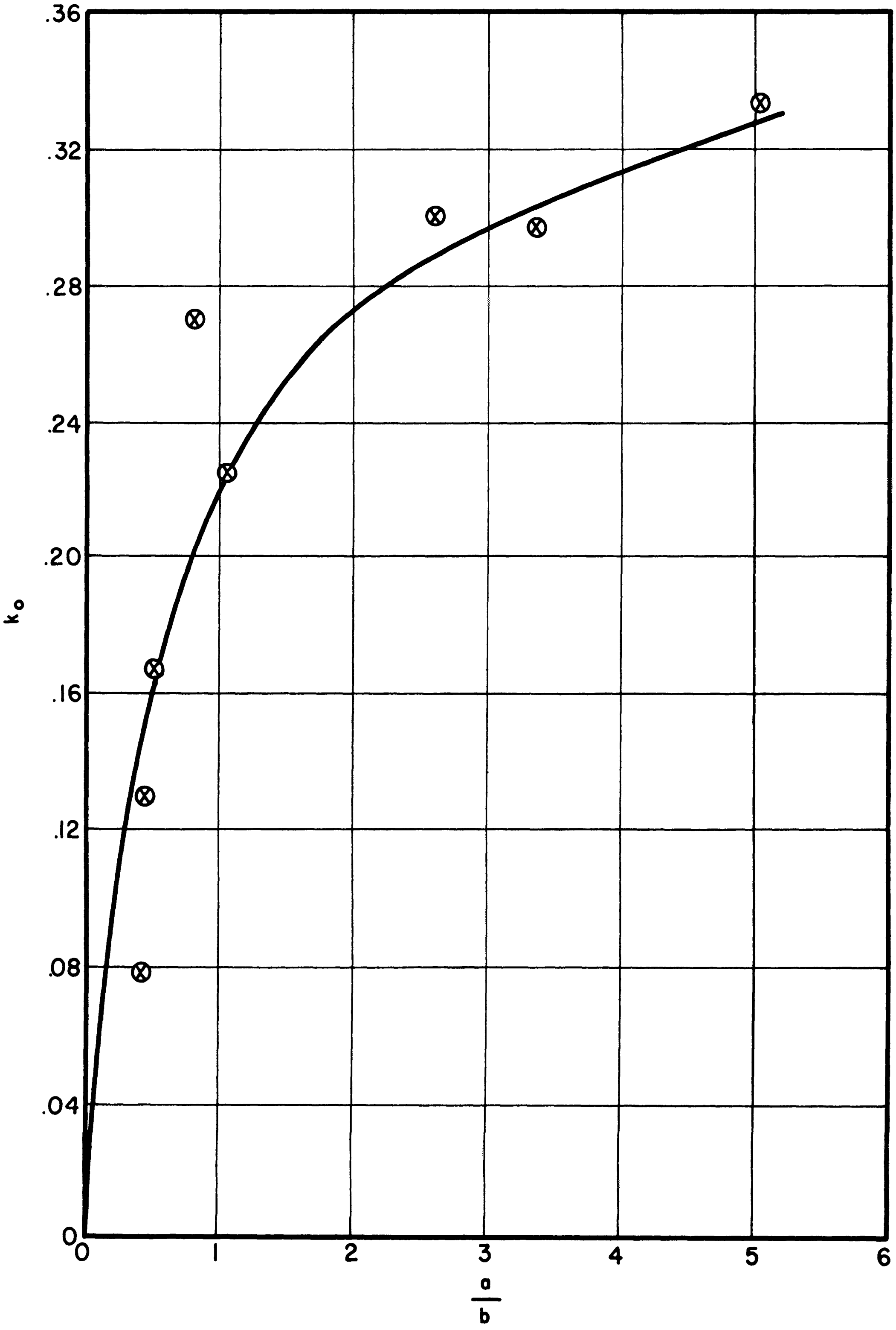


Figure 20

k_o as a Function of $\frac{a}{b}$ for the Reactions Between Emersol 233 LL Elaine and Glycerol at 205°C Where Either the Acid or Glycerol was Added in Steps



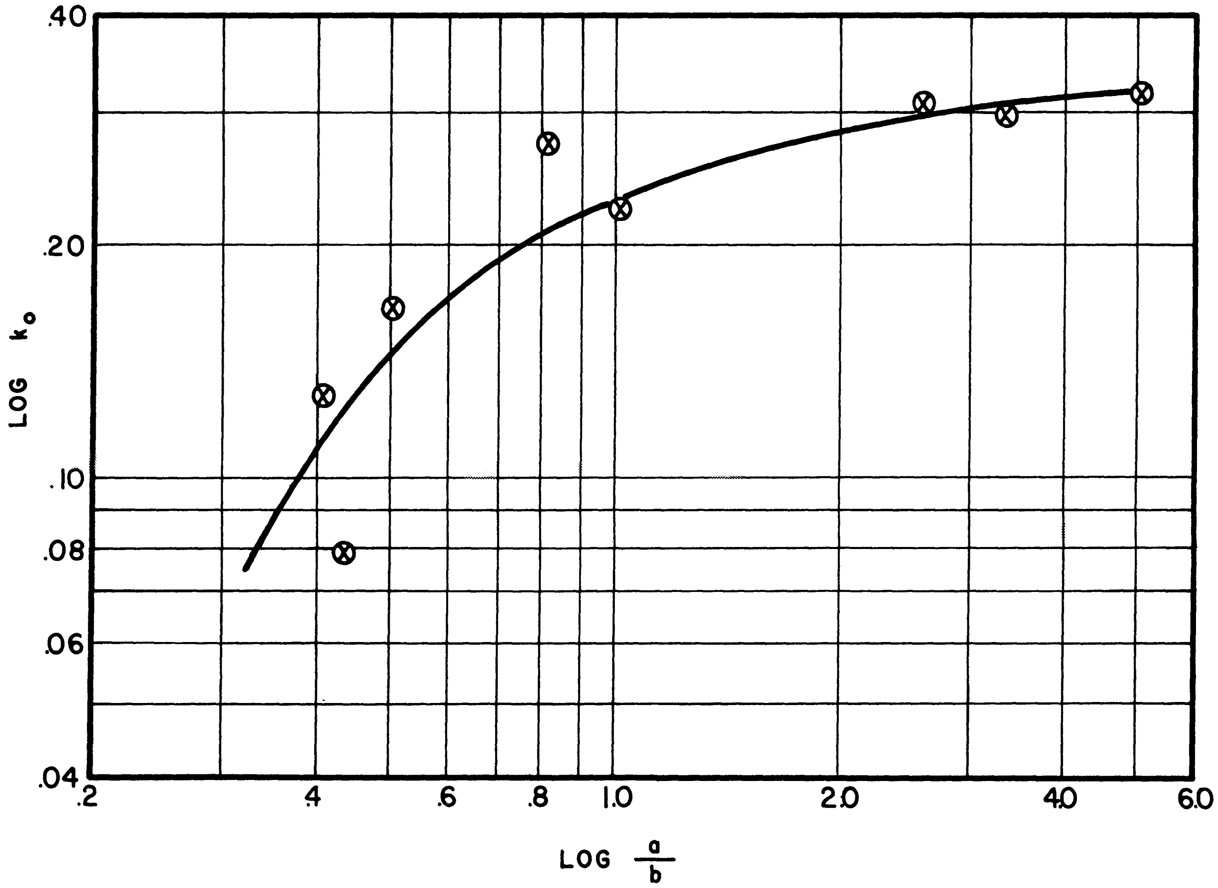


Figure 21

Log k_0 as a Function of Log $\frac{a}{b}$ for the Reactions Between Emersol 233 LL Elaine and Glycerol at 205°C Where Either the Acid or Glycerol was Added in Steps

Equation 8 says that the reaction rate constant is made up of two terms, one of which is independent of concentration while the other is dependent upon the reciprocal of the initial glycerol concentration. On the other hand, equation 9 says that what has been called the reaction rate constant up to now is in reality the product of the true reaction rate constant and the reciprocal of the initial glycerol concentration raised to the γ power. According to Figure 20, γ is not equal to α as was presumed in equation 6.

It is presumable that both k' and k" in equation 8 could vary with temperature. Certainly k', which is the intercept, will vary with temperature. But k" may or may not vary with temperature. Only further investigation can determine this. This does show that the assumption that k_o varied directly with the $\frac{1}{b}$ ratio was not erroneous when the narrow range initially investigated was considered.

The constant, k, in equation 9 will certainly vary with temperature, for if this equation for the rate constant is used the rate equation appears as follows:

$$-\frac{d(a-x)}{dt} = k\left(\frac{1}{b}\right)^{\gamma}\Big((a-x)(b-x)\Big)^{\alpha} \qquad (10)$$

Thus, in this case k would be the true rate constant and $(\frac{1}{b})^{\gamma}$ one of the variables in the equation. Since this makes $\frac{1}{b}$ appear as a variable, γ would not be expected to change with temperature. Once again this hypothesis can only be proven or disproven definitely by experiments at other temperatures.

The values of k', k", k and γ were calculated by means of the least squares method for determining slopes and intercepts.

$k' = 0.0559$

$k'' = 0.0195$

$k = 0.0719$

$\gamma = 0.64$

In conclusion, the study of these two reactions has demonstrated the following:

1. No simple relationship exists between k_o, the reaction rate constant, and the ratio $\frac{a}{b}$.
2. The reaction rate constant can be related to the ratio, $\frac{1}{b}$, by either of the following expressions:

   $k_o = k' + \frac{k''}{b}$ Eq. 8

   or $k_o = k\,(\frac{1}{b})^{\gamma}$ Eq. 9
3. The constants in these equations, k', k'', k and γ may or may not vary with temperature. It appears from the limited data obtained that k' and k are very definitely temperature dependent while k'' may be temperature dependent. But, on the other hand, the data is insufficient to allow any definite hypothesis to be made about the temperature dependence of k''. It seems logical to assume that the constant, γ, is independent of temperature but again the data is not entirely sufficient to prove this theory.

The total result of this investigation has been the development of these two rate equations:

$$-\frac{d(a-x)}{dt} = k\,(\frac{1}{b})^{\gamma}\Big((a-x)(b-x)\Big)^{\alpha} \qquad (10)$$

and

$$-\frac{d(a-x)}{dt} = \left(k' + \frac{k''}{b}\right)\Big((a-x)(b-x)\Big)^{\alpha} \qquad (11)$$

If the exponential constant γ in equation 10 is assumed to be temperature independent, then the value of the rate constant k can be determined for each reaction. Next a plot of log k against $\frac{1}{T}$ can be made to determine whether or not this constant obeys the Arrhenius Equation. If the rate constant obeys this rule, it may be safely assumed that γ is temperature independent. On the other hand if the reaction rate constant does not obey this rule it may be assumed that γ is somewhat dependent upon temperature.

Similarly, k" may be assumed to be temperature independent and k' calculated from the reaction rate data. Then if k' obeys the Arrhenius Equation the assumption that k" is temperature independent may be assumed to be correct and incorrect if the rate constant, k', does not obey this Equation.

Tabulated in Table 9 are the values of the rate constants k' and k for each of the reactions studied, assuming γ and k" are independent of temperature. Figure 22 is an Arrhenius plot of log k' against $\frac{1}{T}$ while Figure 23 is a similar plot of log k against $\frac{1}{T}$.

Examination of Figure 22 reveals that, although the points will fit a straight line, the points are very badly scattered and it is very difficult to determine just where the straight line should be drawn through the points. This indicates that the rate constants obtained from equation 11 although appearing to obey the Arrhenius Equation are apparently not valid in the strictest sense of the word. That is, the data can be forced to fit the equation, but the fit is only a poor approximation and no reliability can be placed on the constants obtained.

Table 9

Reaction Rate Constants k' and k Calculated
According to Equations 10 and 11
Assuming k" and γ are Temperature Independent

Acid	Temp. °C	$\frac{a}{b}$	$\frac{1}{b}$	k'	k
Stearic	190	1.0000	3.1516	0.0229	0.0405
Stearic	191	.6769	2.2326	.0136	.0341
Stearic	204	.6477	2.1496	.0351	.0472
Stearic	222	1.0000	3.1516	.1455	.0993
Stearic	223	1.0000	3.1516	.1604	.1064
Stearic	227	.6640	2.1959	.1122	.0937
Stearic	244	.6516	2.1603	.2190	.1595
Oleic	199	.6600	2.1711	.0372	.0484
Oleic	199	.9567	3.0093	.0567	.0837
Oleic	218	.6676	2.1925	.0956	.0837
Oleic	218	.9313	2.9377	.1493	.1037
Oleic	234	.9613	3.0276	.2815	.1676
Oleic	240	.6413	2.1186	.2259	.1653
Linoleic	187	.6618	2.1626	.0189	.0373
Linoleic	198	1.0000	3.1114	.0612	.0590
Linoleic	202	1.0691	3.3047	.0870	.0705
Linoleic	208	1.0000	3.1114	.0946	.0751
Linoleic	228	.7332	2.3629	.2006	.1423

Figure 22

Log k' as a Function of $\frac{1}{T}$ for Reaction Between Stearic, Oleic and Linoleic Acid and Glycerol

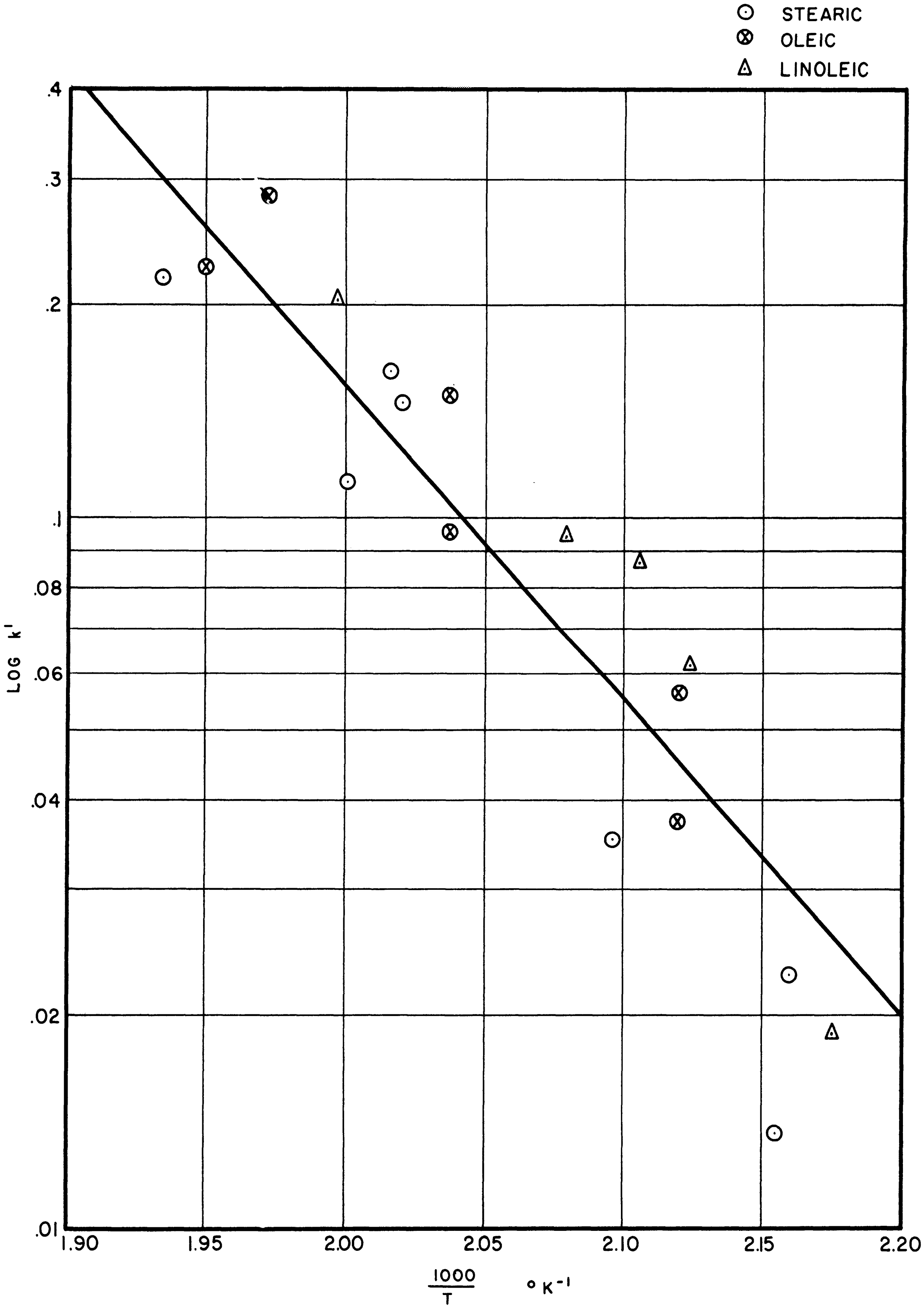


Figure 23

Log k as a Function of $\frac{1}{T}$ for Reaction Between Stearic, Oleic and Linoleic Acid and Glycerol

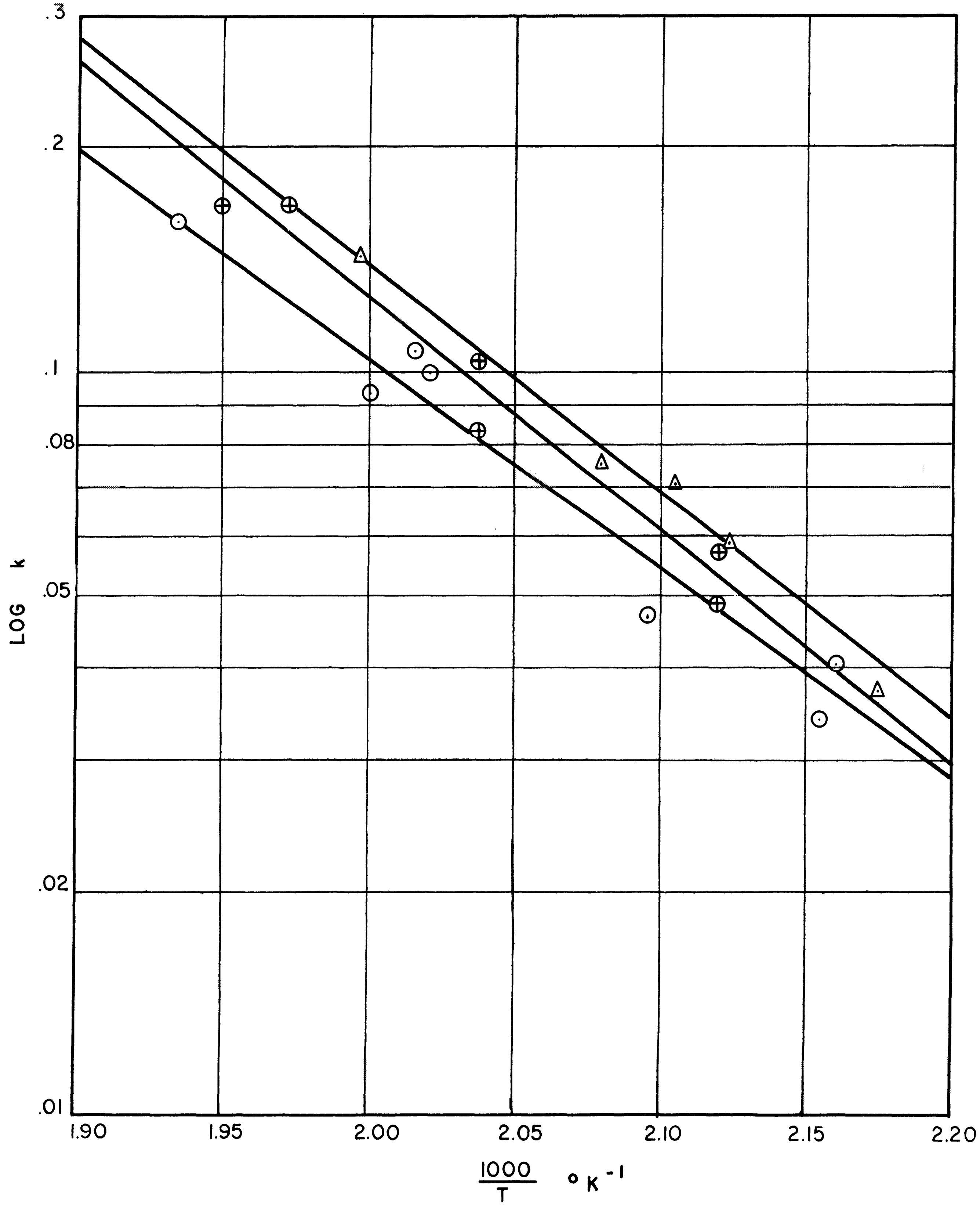


Figure 23, on the other hand, shows that the calculated reaction rate constants obey the Arrhenius Equation very nicely when equation 10 is used to correltate the data. If Figure 23 is compared with Figures 10 and 12 it is seen that each of these three reaction rate constants obey the Arrhenius Equation almost equally well. This indicates very definitely that the rate equation which is most valid over the range of data taken is:

$$-\frac{d(a-x)}{dt} = k\left(\frac{1}{b}\right)^{\gamma}\Big((a-x)(b-x)\Big)^{\alpha} \qquad (10)$$

where the value of γ is not certain. HOwever, within the narrow range of data initially taken $(2.0 < \frac{1}{b} < 3.3)$ the value of γ appears to be in the range $1.0 < \gamma < 1.2$, while over an extended range of $\frac{1}{b}$ values $(1.5 < \frac{1}{b} < 15)$ γ appeared to have a value of 0.64. Therefore, it is apparently safe to assume that $0.64 < \gamma\ 1.2$. Thus perhaps γ may set equal to unity as indicated in equation 4 in order to simplify calculations.

The Activation Energies, E_o, and the "collision factors", A, were calculated for the three acids using this correlation and are listed in Table 10 along with the Activation Energies and "collision factors" obtained using the rate constants from equations (4) and (6).

Looking at Table 10, the values of E_o and A are not changed very much by a change in γ. The largest change caused by a change in γ is the "collision factor" for linoleic acid which is decreased by a factor of two as γ is increased from 0.64 to 1.2. Thus it appears that the value of γ is not critical and for all practical purposes may be assumed to be unity.

Table 10

Activation Energies and "Collision Factors" Using Rate Constants From Equations 4, 6, and 10

Acid	k from Eq. 10 $\gamma = .64$ A	E_o	k_1 from Eq. 4 $\gamma = 1.0$ A	E_o	k_3 from Eq. 6 $\gamma = 1.2$ A	E_o
Stearic	6.47×10^4	13,300	5.95×10^4	13,500	7.50×10^4	13,900
Oleic	2.99×10^5	14,600	2.49×10^5	14,800	2.96×10^5	15,100
Linoleic	2.51×10^5	14,300	1.62×10^5	14,200	1.29×10^5	14,200

If γ is assumed to be unity, the rate equations for each acid used are as follows:

Stearic Acid

$$-\frac{d(a-x)}{dt} = 5.95 \times 10^4 \, e^{-13,500/RT} \left(\frac{1}{b}\right)\left((a-x)(b-x)\right)^{1.2}$$

Oleic Acid

$$-\frac{d(a-x)}{dt} = 2.49 \times 10^5 \, e^{-14,800/RT} \left(\frac{1}{b}\right)\left((a-x)(b-x)\right)^{1.2}$$

Linoleic Acid

$$-\frac{d(a-x)}{dt} = 1.62 \times 10^5 \, e^{-14,200/RT} \left(\frac{1}{b}\right)\left((a-x)(b-x)\right)^{1.2}$$

As seen previously the data of Feuge, Kraemer and Bailey (17) can be correlated by Equations 4, 5, 6 or 7. It follows directly, then, that their data can be correlated according to Equation 10, which is the same as Equation 4 when $\gamma = 1$. An attempt was also made to correlate the data of the Northwestern Production Club (36) using Equation 10. The reaction studied by them was between soybean fatty acids and diglycerol. The results of this correlation are shown in Appendix E. As is seen in

Appendix E this data can be correlated very well by Equation 10. Thus the mechanism of diglycerol esterification is similar to the mechanism of glycerol esterification.

IV. CONCLUSIONS

An investigation of the kinetics of the esterification of glycerol with stearic, oleic and linoleic acids has been made. The results of this investigation have been discussed and from these results the following conclusions have been made.

A rate equation has been developed which is valid over a wide range of operating conditions. This equation was valid for all three acids used. Written in general form this equation is:

$$-\frac{d(a-x)}{dt} = k\left(\frac{1}{b}\right)^{\gamma}\Big((a-x)(b-x)\Big)^{\alpha}$$

The exponential constant, α, was found to lie between the limits 1.12 and 1.23 with an average value of 1.18. This indicates that the mechanism of the reaction is complex, and that the mechanism does not change with a change in the degree of saturation of the acids.

The value of the other exponential constant, γ, was found to vary quite widely (0.64 to 1.20) but it was also demonstrated that its value was not critical. That is, a change in γ would only cause a change in k for any particular reaction and the change in k would be much less than the change in γ.

The initial phase of the investigation, during which $2.0 < \frac{1}{b} < 3.3$, indicated that γ could be set equal to 1.0 or α with equally good results being obtained. The final part of the investigation, where $1.5 < \frac{1}{b} < 15$, indicated that $\gamma = 0.64$. The use of this value of γ in the data from the initial phase produced acceptable results. Thus, the value of γ did not appear to be critical and for all practical purposes could be assumed to be unity.

The reaction rate constant, k, varied both with the degree of unsaturation of the acids and with temperature. For each acid k obeyed the Arrhenius Equation $k = Ae^{-E_0/RT}$,

which relates k to a function of the absolute temperature. The variation of k with unsaturation was slight and could be ignored if so desired. The Activation Energies, E_0, of all three acids were almost the same. Therefore, most of the variation was in the "collision factors", A. This indicates that the unsaturated acids may collide more or have slightly more "efficient" collisions than the saturated acids.

The fact that the reaction rate was inversely proportional to the initial glycerol concentration indicates that the reaction products were inhibiting the reaction (29). This, too, indicates that the reaction mechanism must be complex. Thus, no reaction mechanism can be predicted from data on the acid concentration alone. Instead, data on the concentration of free glycerol, monoglycerides, diglycerides and triglycerides is needed to determine the reaction mechanism. These concentrations could not be measured during this investigation because only limited quantities of pure acids were available. However, this investigation has shown that the reaction mechanism must be similar for all three acids, so in future studies a mixture of these acids may be used to run reactions of sufficient size to allow large samples to be taken and the above concentrations measured.

The rate equation developed during this investigation was used to correlate previous kinetic data on the reactions of mixed acids with glycerol and diglycerol. The results were similar to those obtained by the writer.

Even though a complete understanding of the mechanism of glycerol esterification has not been made possible by this study, a rate expression has been developed which will accurately predict the esterification rate. Only through more thorough investigations will a complete understanding of this reaction mechanism be understood.

APPENDICES

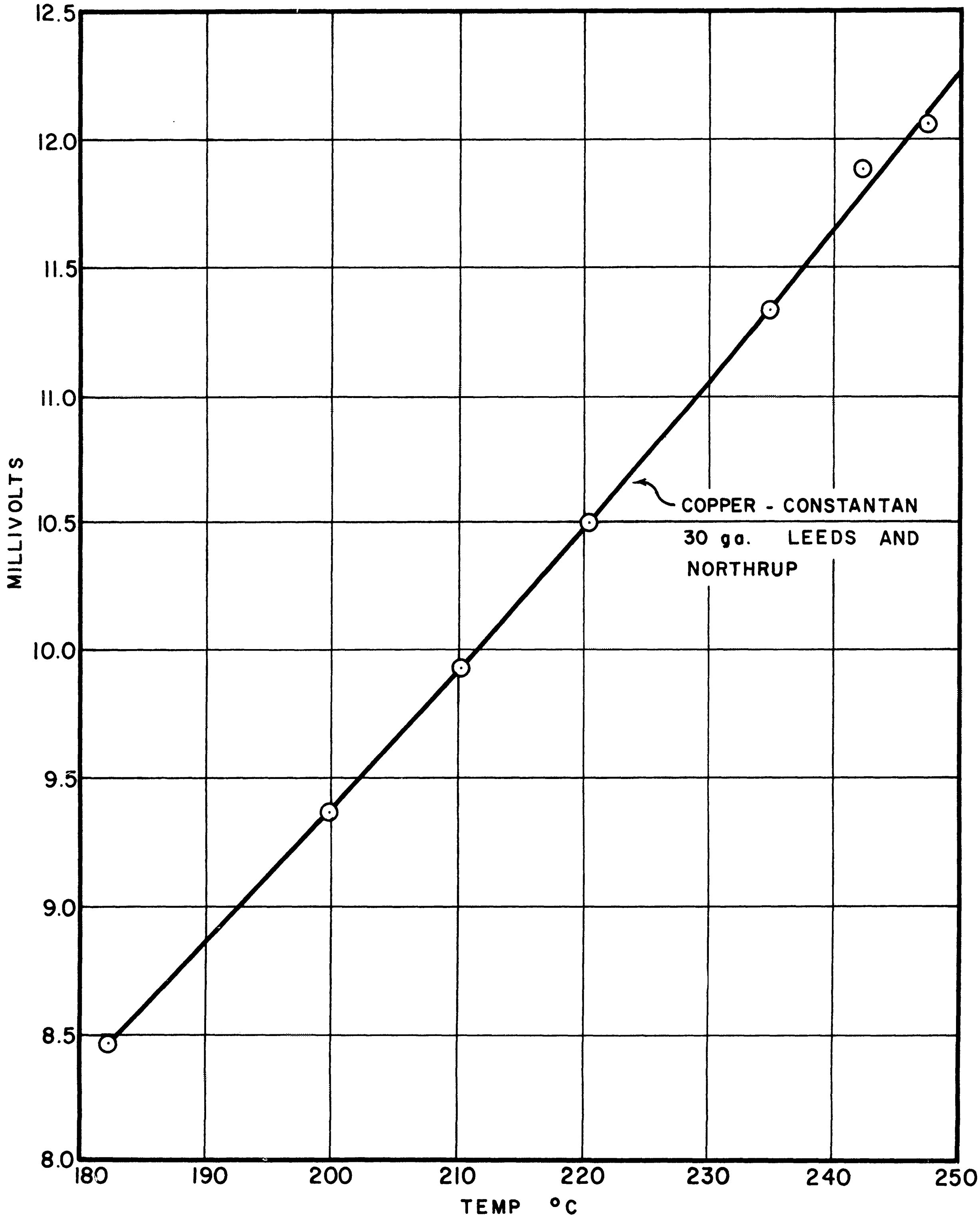
APPENDIX A

THERMOCOUPLE CALIBRATION

The thermocouple used to measure the reaction temperature was a 30 gauge copper-constantan thermocouple manufactured by Leeds and Northrup. The thermocouple and potentiometer were calibrated against a standard mercury thermometer. A reference junction of 0°C was maintained by immersing the cold junction of the thermocouple in melting ice. The calibration curve is given in Figure 24.

Figure 24

Thermocouple Calibration



APPENDIX B

SAMPLE CALCULATION AND CORRELATION OF DATA ACCORDING TO EQUATION 3

The data for this sample calculation were taken from the reaction between oleic acid and glycerol at 218°C using 50% equivalent excess glycerol. A weighed amount of each sample was titrated against a standardized KOH in methanol solution to a phenolphthalein endpoint.

The KOH solution was standardized against a weighed sample of primary standard grade benzoic acid.

$$\text{Normality of KOH} = \frac{\text{g. benzoic acid}}{\text{Eq. wt. benzoic acid}} \times \frac{1000}{\text{ml KOH}}$$

and for this reaction

$$N = \frac{0.5279}{122.05} \times \frac{1000}{41.45} = 0.1043\ N$$

It was proven in the section on Apparatus and Procedures that

$$\frac{\text{eq. Free Acid}}{\text{100 gm. mixture}} = \frac{\text{ml 0.1 N KOH}}{\text{gm. mixture}} \times \frac{1}{100}$$

Therefore, if a KOH solution of 0.1043 N is used

$$\frac{\text{eq. Free Acid}}{\text{100 gm mixture}} = \frac{\text{ml 0.1043 N KOH}}{\text{gm}} \times \frac{0.1043}{0.1000} \times \frac{1}{100}$$

$$= \frac{\text{ml 0.1043 N KOH}}{\text{gm}} \times \frac{1.043}{100}$$

Listed in Table 11 is the raw data taken for this reaction.

The theoretical amount of KOH required at $t \doteq 0$ is calculated as follows:

$$\frac{\text{200.2 gm Acid}}{\text{232.8 gm mixture}} \times 100 = 86.00 \text{ percent Acid by wt.}$$

Table 11

Raw Data Taken from Reaction between Oleic Acid and Glycerol
at 218°C Using 50 Percent Excess Glycerol

Time min.	Gross Weight gm	Tare gm	Net Sample Wt. gm	Final Buret Reading ml	Initial Buret Reading ml	Net ml KOH Used	Ml .1043 N KOH per gm	Ml 0.1 N KOH per gm
0	22.5612	21.4624	1.0988	32.07	0.00	32.07	29.15	30.40
5	21.3259	19.7168	1.6091	40.96	0.00	40.96	25.39	26.48
10	21.0009	19.1796	1.8213	38.40	0.00	38.40	21.08	21.99
15	20.2933	19.0956	1.1977	21.70	0.00	21.70	18.12	18.90
25	20.7685	19.3386	1.4299	19.50	0.00	19.50	13.64	14.23
35	20.2704	18.8573	1.4131	35.50	19.95	15.55	11.00	11.47
45	20.0480	18.7504	1.2976	12.20	0.00	12.20	9.40	9.81
60	20.7694	19.2680	1.5014	23.80	12.55	11.25	7.49	7.82
75	20.7091	19.1932	1.5159	33.10	24.00	9.10	6.00	6.26
90	20.8208	19.4761	1.3449	39.55	33.30	6.25	4.65	4.85
120	20.7109	19.2487	1.4622	44.20	39.74	4.46	3.05	3.18
150	21.0735	19.6185	1.4550	3.10	0.00	3.10	2.13	2.22
180	20.6598	19.2568	1.4030	5.80	3.50	2.30	1.64	1.70
210	21.2728	19.7552	1.5176	8.00	6.00	2.00	1.32	1.38
240	20.6037	19.1180	1.4857	9.68	8.20	1.48	1.00	1.04
270	20.4077	19.0373	1.3704	10.95	9.88	1.07	0.78	0.81

$$\frac{86.00\text{ gm Acid}}{100\text{ gm mixture}} \times \frac{1\text{ eq. Acid}}{282.44\text{ gm Acid}} = 0.3045\ \frac{\text{eq. Acid}}{100\text{ gm}}$$

$$\frac{0.3045\text{ eq. Acid}}{100\text{ gm}} \times 100 = \frac{30.45\text{ ml }0.1\text{ N KOH}}{\text{gm mixture}}$$

In the analysis for free acid only 30.40 ml 0.1 N KOH were used per gram of initial material. Since the initial sample was taken slightly after t = 0.00 this lower result should have been expected. For the remainder of the calculations, the calculated value of 30.45 will be used.

The initial concentration of glycerol is:

$$\frac{32.6\text{ gm glycerol}}{232.8\text{ gm mixture}} \times 100 = 14.00\text{ percent Glycerol by wt.}$$

or

$$\frac{14.00\text{ gm glycerol}}{100\text{ gm mixture}} \times \frac{1\text{ eq. glycerol}}{30.70\text{ gm glycerol}} = 0.4561\ \frac{\text{eq. glycerol}}{100\text{ gm}}$$

The concentration of glycerol at any time can be calculated from the measured concentration of acid as follows:

$$(a-x) + b - a = (b-x)$$

or

$$(a-x) + 0.4561 - 0.3045 = (a-x) + 0.1516 = (b-x)$$

To smooth the data $-\frac{\Delta(a-x)}{\Delta t}$ must be calculated for each time interval. This is done as follows for each time interval:

$$-\frac{\Delta(a-x)}{\Delta t} = \frac{(a-x)_2 - (a-x)_1}{t_2 - t_1}$$

From a plot of $-\frac{\Delta(a-x)}{\Delta t}$ against t (see Figure 7) the instantaneous rate of reaction $-\frac{d(a-x)}{dt}$ can be determined by drawing a smooth curve through the plateaus formed from the plotting of $-\frac{\Delta(a-x)}{\Delta t}$ against t. This smooth curve should be drawn so that the area between the curve and the plateaus is equal to the area between the plateaus and the curve.

Next the product (a-x)(b-x) can be obtained by multiplying the values of (a-x) and (b-x) obtained by the process described above. Table 12 represents a step-by-step calculation of (a-x)(b-x) and $-\frac{\Delta(a-x)}{\Delta t}$ and finally $-\frac{d(a-x)}{dt}$.

The next step in the calculations was to plot $\log\left[-\frac{d(a-x)}{dt}\right]$ against $\log[(a-x)(b-x)]$, (Figure 9), and measure the slope and intercept of the straight line obtained. The slope and intercept were determined using the method of least squares. The details of how the least squares method was applied are given in Appendix D.

Table 12

Step by Step Determination of (a-x)(b-x) and
$-\frac{d(a-x)}{dt}$ for Reaction Between Oleic Acid and Glycerol
at 218°C Using 50% Excess Glycerol

t min.	(a-x) $\frac{\text{eq. Acid}}{\text{100 gm}}$	(b-x) $\frac{\text{eq. OH}}{\text{100 gm}}$	(a-x)(b-x)	$-\frac{\Delta(a-x)}{\Delta t}$	$-\frac{d(a-x)}{dt}$ from Fig. 7
0	0.3045	0.4561	0.1389		
				0.00794	
5	.2648	.4164	.1103		
				.00898	
10	.2199	.3715	.0817		0.00685
				.00618	
15	.1890	.2406	.0644		.00565
				.00467	
25	.1423	.2939	.0418		.00342
				.00276	
35	.1147	.2663	.0305		.00223
				.00166	
45	.0981	.2497	.0245		.00168
				.00133	
60	.0782	.2298	.0180		.00120
				.00104	
75	.0626	.2142	.0134		.00092
				.00094	
90	.0485	.2001	.0097		.00068
				.00056	
120	.0318	.1834	.0058		.00040
				.00032	
150	.0222	.1738	.0039		.00023
				.00017	
180	.0171	.1687	.0029		.00013
				.00011	
210	.0138	.1654	.0023		.00011
				.00011	
240	.0104	.1620	.0017		.00008
				.00008	
270	.0081	.1597	.0013		.00006

APPENDIX C

Compilation of Data

This appendix contains the data taken during this investigation in the form of plots of $\log\left[-\frac{d(a-x)}{dt}\right]$ against $\log\left[(a-x)(b-x)\right]$ and in the form of tables containing the values of $(a-x)$, $(b-x)$, $(a-x)(b-x)$ and $-\frac{d(a-x)}{dt}$.

Tables 13 through 19 contain the data on the reactions between stearic acid and glycerol, Tables 20 through 25 contain the data on the reactions between oleic acid and glycerol and Tables 26 through 30 contain the data on the reactions between linoleic acid and glycerol.

Figure 25 represents a plot of $\log\left[-\frac{d(a-x)}{dt}\right]$ against $\log\left[(a-x)(b-x)\right]$ for the reactions between stearic acid and glycerol, Figure 26 is the same plot for the reactions between oleic acid and glycerol and Figure 27 is the plot for the reactions between linoleic acid and glycerol.

Table 13

Data on Reaction Between Stearic Acid and Glycerol at 190°C

Time min.	(a-x) $\frac{\text{eq. Acid}}{\text{100 gm}}$	(b-x) $\frac{\text{eq. OH}}{\text{100 gm}}$	(a-x)(b-x)	$-\frac{d(a-x)}{dt}$ $\frac{\text{eq.}}{\text{100 gm min}}$
0	0.3173	0.3173	0.1007	
5	.3036	.3036	.0922	0.00428
10	.2831	.2831	.0801	.00376
15	.2669	.2669	.0712	.00322
20	.2484	.2484	.0617	.00276
30	.2268	.2268	.0514	.00212
40	.2051	.2051	.0421	.00169
50	.1907	.1907	.0364	.00142
60	.1759	.1759	.0309	.00119
70	.1647	.1647	.0271	.00102
80	.1552	.1552	.0241	.00087
100	.1420	.1420	.0202	.00067
120	.1294	.1294	.0167	.00054
150	.1162	.1162	.0135	.00042
180	.1044	.1044	.0109	.00033
210	.0961	.0961	.0092	.00026
240	.0891	.0891	.0079	.00021
300	.0793	.0793	.0063	.00015
360	.0714	.0714	.0051	.00013

Table 14

Data on Reaction Between Stearic Acid and Glycerol at 191°C

Time min.	(a-x) $\frac{\text{eq. Acid}}{\text{100 gm}}$	(b-x) $\frac{\text{eq. OH}}{\text{100 gm}}$	(a-x)(b-x)	$-\frac{d(a-x)}{dt}$ $\frac{\text{eq}}{\text{100 gm min}}$
0	0.3032	0.4479	0.1358	
5	.2910	.4357	.1268	
10	.2660	.4107	.1092	0.00403
15	.2496	.3939	.0982	.00364
20	.2298	.3745	.0861	.00326
25	.2148	.3595	.0772	.00292
30	.2005	.3452	.0692	.00257
35	.1891	.3338	.0631	.00228
40	.1778	.3225	.0573	.00206
50	.1588	.3035	.0482	.00171
60	.1428	.2875	.0411	.00143
70	.1304	.2751	.0359	.00121
80	.1192	.2639	.0315	.00105
100	.0992	.2439	.0242	.00082
120	.0849	.2296	.0195	.00063
150	.0721	.2168	.0156	.00042
180	.0594	.2041	.0121	.00031
210	.0514	.1961	.0101	.00025
240	.0440	.1887	.0083	.00022

Table 15

Data on Reaction Between Stearic Acid and Glycerol at 204°C

Time min.	(a-x) eq. Acid / 100 gm	(b-x) eq. OH / 100 gm	(a-x)(b-x)	$-\frac{d(a-x)}{dt}$ eq / 100 gm min
0	0.3013	0.4652	0.1402	0.00775
5	.2671	.4310	.1151	.00658
10	.2418	.4057	.0981	.00557
15	.2189	.3828	.0838	.00435
20	.2019	.3658	.0739	.00358
30	.1752	.3391	.0594	.00266
40	.1464	.3103	.0454	.00207
50	.1293	.2932	.0379	.00167
60	.1142	.2781	.0318	.00137
80	.0911	.2550	.0232	.00100
100	.0741	.2380	.0177	.00074
120	.0611	.2250	.0137	.00056
150	.0473	.2112	.0100	.00039
180	.0371	.2010	.0075	.00027
210	.0297	.1936	.0058	.00019
240	.0246	.1885	.0046	.00013

Table 16

Data on Reaction Between Stearic Acid and Glycerol at 222°C

Time min.	(a-x) $\frac{\text{eq. Acid}}{\text{100 gm}}$	(b-x) $\frac{\text{eq. OH}}{\text{100 gm}}$	(a-x)(b-x)	$-\frac{d(a-x)}{dt}$ $\frac{\text{eq}}{\text{100 gm min}}$
0	0.3173	0.3173	0.1007	
4	.2745	.2745	.0735	0.00940
8	.2391	.2391	.0572	.00700
12	.2131	.2131	.0454	.00560
16	.1942	.1942	.0377	.00420
20	.1772	.1772	.0314	.00335
25	.1622	.1622	.0263	.00266
30	.1476	.1476	.0218	.00213
40	.1297	.1297	.0168	.00156
50	.1148	.1148	.0132	.00120
60	.1043	.1043	.0109	.00097
70	.0954	.0954	.0091	.00079
80	.0882	.0882	.0078	.00067
100	.0764	.0764	.0058	.00050
120	.0705	.0705	.0050	.00039
150	.0619	.0619	.0038	.00028
180	.0557	.0557	.0031	.00021
210	.0507	.0507	.0026	.00017
240	.0476	.0476	.0023	.00014

Table 17

Data on Reaction Between Stearic Acid and Glycerol at 223°C

Time min.	(a-x) $\frac{\text{eq. Acid}}{\text{100 gm}}$	(b-x) $\frac{\text{eq. OH}}{\text{100 gm}}$	(a-x)(b-x)	$-\frac{d(a-x)}{dt}$ $\frac{\text{eq}}{\text{100 gm min}}$
0	0.3173	0.3173	0.1007	0.01100
4	.2814	.2814	.0792	.00879
8	.2420	.2420	.0586	.00605
12	.2069	.2069	.0428	.00436
16	.1897	.1897	.0360	.00357
20	.1782	.1782	.0318	.00302
25	.1622	.1622	.0263	.00251
30	.1518	.1518	.0230	.00213
35	.1419	.1419	.0201	.00184
40	.1333	.1333	.0178	.00161
50	.1187	.1187	.0141	.00125
60	.1084	.1084	.0118	.00099
70	.1006	.1006	.0101	.00078
80	.0923	.0923	.0085	.00065
100	.0828	.0828	.0069	.00047
120	.0739	.0739	.0055	.00037
150	.0654	.0654	.0043	.00027
180	.0600	.0600	.0036	.00020
210	.0547	.0547	.0030	.00017
240	.0517	.0517	.0027	.00014

Table 18

Data on Reaction Between Stearic Acid and Glycerol at 227°C

Time min.	(a-x) eq. Acid / 100 gm	(b-x) eq. OH / 100 gm	(a-x)(b-x)	$-\frac{d(a-x)}{dt}$ eq / 100 gm min
0	0.3024	0.4554	0.1337	
5	.2450	.3980	.0975	0.01065
10	.2048	.3578	.0733	.00804
15	.1728	.3258	.0563	.00564
20	.1496	.3026	.0453	.00413
25	.1308	.2838	.0371	.00337
30	.1163	.2693	.0313	.00279
40	.0923	.2453	.0226	.00198
50	.0775	.2305	.0179	.00146
60	.0639	.2169	.0139	.00110
70	.0551	.2081	.0115	.00083
80	.0471	.2001	.0094	.00069
100	.0353	.1883	.0066	.00049
120	.0266	.1796	.0048	.00035
150	.0196	.1726	.0034	.00019
180	.0144	.1674	.0024	.00013
210	.0106	.1636	.0017	.00008

Table 19

Data on Reaction Between Stearic Acid and Glycerol at 244°C

Time min.	(a-x) $\frac{\text{eq. Acid}}{\text{100 gm}}$	(b-x) $\frac{\text{eq. OH}}{\text{100 gm}}$	(a-x)(b-x)	$-\frac{d(a-x)}{dt}$ $\frac{\text{eq}}{\text{100 gm min}}$
0	0.3016	0.4629	0.1396	
2Z	.2516	.4129	.1039	0.01960
4	.2193	.3806	.0835	.01495
6	.1971	.3584	.0706	.01235
8	.1746	.3359	.0587	.00983
10	.1572	.3185	.0501	.00805
15	.1229	.2842	.0349	.00534
20	.1004	.2617	.0263	.00384
25	.0847	.2460	.0209	.00293
30	.0704	.2317	.0163	.00230
40	.0528	.2141	.0113	.00150
50	.0413	.2026	.0084	.00109
60	.0320	.1933	.0062	.00077
70	.0258	.1871	.0048	.00057
80	.0212	.1825	.0039	.00045
100	.0137	.1750	.0024	.00024
120	.0101	.1714	.0017	.00016
140	.0072	.1685	.0012	.00011

Figure 25

Plot of $\mathrm{Log}\left[-\frac{d(a-x)}{dt}\right]$ Against Log(a-x)(b-x) for the Reactions Between Stearic Acid and Glycerol.

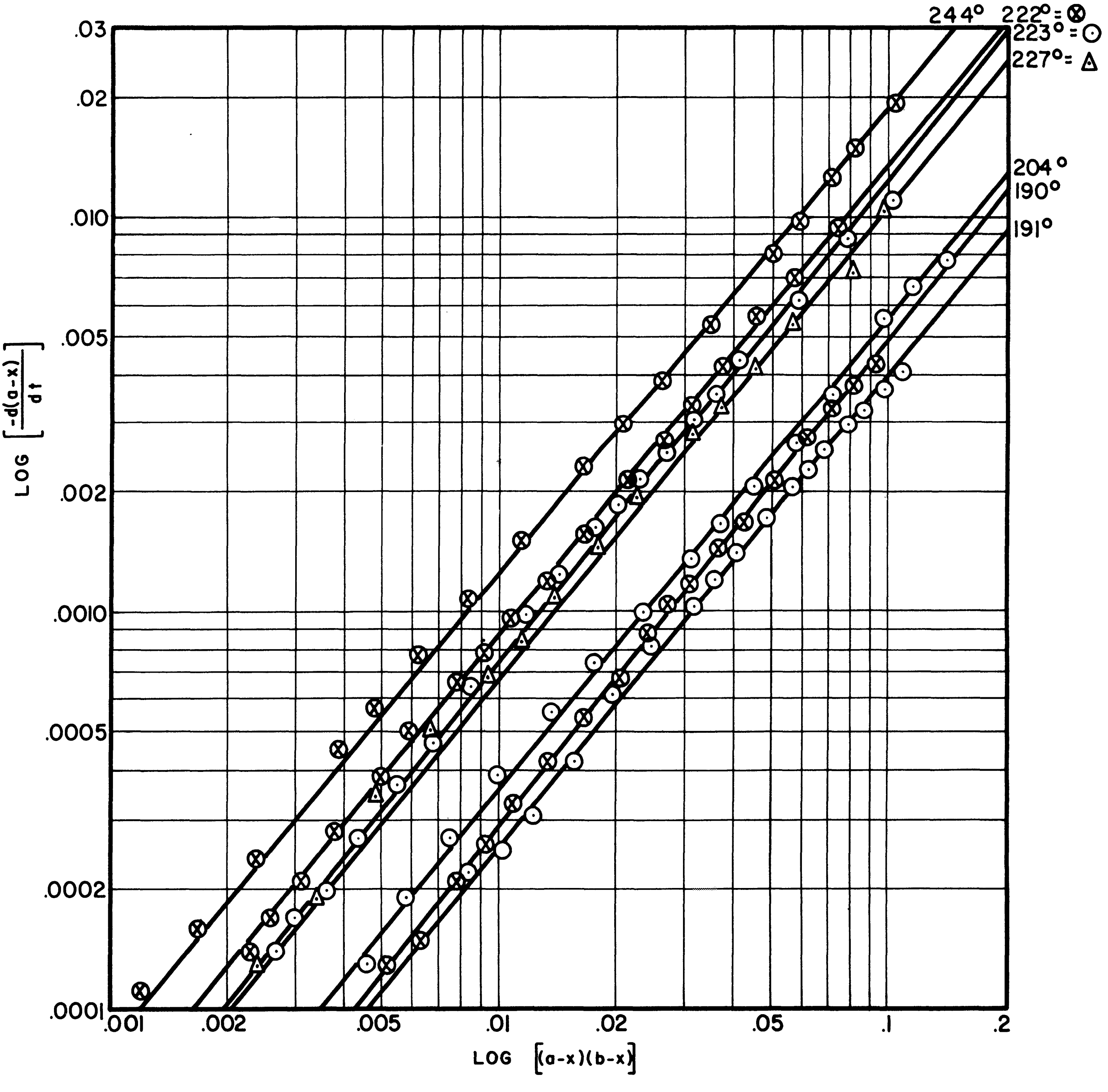


Table 20

Data on Reaction Between Oleic Acid and Glycerol at 199°C

Time min.	(a-x) $\frac{\text{eq. Acid}}{\text{100 gm}}$	(b-x) $\frac{\text{eq. OH}}{\text{100 gm}}$	(a-x)(b-x)	$-\frac{d(a-x)}{dt}$ $\frac{\text{eq}}{\text{100 gm min}}$
0	0.3040	0.4606	0.1400	
5	.2800	.4366	.1222	0.00700
10	.2487	.4053	.1008	.00525
15	.2268	.3834	.0870	.00407
25	.1907	.3473	.0662	.00295
35	.1670	.3236	.0540	.00223
45	.1428	.2994	.0428	.00177
60	.1203	.2769	.0333	.00131
75	.1027	.2593	.0266	.00099
90	.0898	.2464	.0221	.00078
105	.0789	.2355	.0186	.00063
120	.0714	.2280	.0163	.00052
150	.0564	.2130	.0120	.00038
180.5	.0458	.2024	.0093	.00030
210.7	.0378	.1943	.0073	.00025
240	.0311	.1877	.0058	.00018
270	.0263	.1829	.0048	.00013
300	.0224	.1790	.0040	.00010
330	.0195	.1761	.0034	.00008

Table 21

Data on Reaction Between Oleic Acid and Glycerol at 199°C

Time min.	(a-x) $\frac{\text{eq. Acid}}{\text{100 gm}}$	(b-x) $\frac{\text{eq. OH}}{\text{100 gm}}$	(a-x)(b-x)	$-\frac{d(a-x)}{dt}$ $\frac{\text{eq}}{\text{100 gm min}}$
0	0.3179	0.3323	0.1056	0.00765
5	.2845	.2989	.0850	.00600
10	.2607	.2751	.0717	.00490
15	.2371	.2515	.0571	.00390
20	.2200	.2344	.0516	.00320
25	.1995	.2139	.0427	.00273
35	.1725	.1869	.0322	.00193
45	.1475	.1619	.0239	.00147
60	.1297	.1441	.0187	.00103
75	.1177	.1321	.0156	.00077
90	.1068	.1212	.0129	.00063
105	.0981	.1125	.0110	.00052
120	.0869	.1013	.0088	.00043
150	.0800	.0944	.0075	.00031
180	.0690	.0834	.0057	.00025
210	.0623	.0767	.0048	.00019
240	.0575	.0719	.0041	.00016
270	.0528	.0672	.0035	.00014
300	.0490	.0634	.0031	.00011
330	.0448	.0592	.0027	.00010

Table 22

Data on Reaction Between Oleic Acid and Glycerol at 218°C

Time min.	(a-x) $\frac{\text{eq. Acid}}{\text{100 gm}}$	(b-x) $\frac{\text{eq. OH}}{\text{100 gm}}$	(a-x)(b-x)	$-\frac{d(a-x)}{dt}$ $\frac{\text{eq}}{\text{100 gm min}}$
0	0.3045	0.4561	0.1389	
5	.2648	.4164	.1103	
10	.2199	.3715	.0817	0.00685
15	.1890	.3406	.0644	.00565
25	.1423	.2939	.0418	.00342
35	.1147	.2663	.0305	.00223
45	.0981	.2497	.0245	.00168
60	.0782	.2298	.0180	.00120
75	.0626	.2142	.0134	.00092
90	.0485	.2001	.0097	.00068
120	.0318	.1834	.0058	.00040
150	.0222	.1738	.0039	.00023
180	.0171	.1687	.0029	.00013
210	.0138	.1654	.0023	.00011
240	.0104	.1620	.0017	.00008
270	.0081	.1597	.0013	.00006

Table 23

Data on Reaction Between Oleic Acid and Glycerol at 218°C

Time min.	$(a-x)$ $\frac{\text{eq. Acid}}{\text{100 gm}}$	$(b-x)$ $\frac{\text{eq. OH}}{\text{100 gm}}$	$(a-x)(b-x)$	$-\frac{d(a-x)}{dt}$ $\frac{\text{eq}}{\text{100 gm min}}$
0	0.3170	0.3404	0.1079	
5.1	.2723	.2957	.0805	0.00890
10	.2338	.2572	.0601	.00730
15	.2017	.2251	.0454	.00575
20	.1759	.1993	.0351	.00410
30	.1440	.1674	.0241	.00252
40	.1220	.1454	.0177	.00175
50	.1072	.1306	.0140	.00132
60	.0955	.1189	.0114	.00105
75	.0824	.1058	.0087	.00078
90	.0727	.0961	.0070	.00060
105	.0647	.0881	.0057	.00048
120	.0575	.0809	.0047	.00039
135	.0523	.0757	.0040	.00032
150	.0482	.0716	.0034	.00028
175	.0423	.0657	.0028	.00023
210	.0344	.0578	.0020	.00015
240	.0307	.0541	.0017	.00012
270	.0286	.0520	.0015	.00009
300	.0261	.0495	.0013	.00007

Table 24

Data on Reaction Between Oleic Acid and Glycerol at 234°C

Time min.	(a-x) $\frac{\text{eq. Acid}}{\text{100 gm}}$	(b-x) $\frac{\text{eq. OH}}{\text{100 gm}}$	(a-x)(b-x)	$-\frac{d(a-x)}{dt}$ $\frac{\text{eq}}{\text{100 gm min}}$
0	0.3181	0.3303	0.1051	
1	.2997	.3119	.0935	
2	.2831	.2953	.0836	
4	.2548	.2670	.0680	0.01200
6	.2328	.2450	.0570	.01010
8	.2126	.2248	.0478	.00835
10	.1961	.2083	.0409	.00725
15	.1624	.1746	.0284	.00505
20	.1427	.1549	.0221	.00360
25	.1272	.1394	.0177	.00283
30	.1143	.1265	.0145	.00232
35	.1039	.1161	.0121	.00190
40	.0960	.1082	.0104	.00155
50	.0827	.0949	.0079	.00112
60	.0742	.0864	.0064	.00084
70	.0676	.0798	.0054	.00063
80	.0612	.0734	.0045	.00050
100	.0537	.0659	.0035	.00035
120	.0482	.0604	.0029	.00027

Table 25

Data on Reaction Between Oleic Acid and Glycerol at 240°C

Time min.	(a-x) $\frac{\text{eq. Acid}}{\text{100 gm}}$	(b-x) $\frac{\text{eq. OH}}{\text{100 gm}}$	(a-x)(b-x)	$-\frac{d(a-x)}{dt}$ $\frac{\text{eq}}{\text{100 gm min}}$
0	0.3027	0.4720	0.1429	
1	.2896	.4589	.1329	
2	.2653	.4346	.1153	
4	.2341	.4034	.0944	0.01550
6	.2341	.3770	.0784	.01310
8	.1872	.3565	.0667	.01150
10	.1697	.3390	.0575	.00984
15	.1304	.2997	.0391	.00590
20	.1069	.2762	.0295	.00400
25	.0890	.2583	.0230	.00305
30	.0718	.2411	.0173	.00238
40	.0534	.2227	.0119	.00146
50	.0426	.2119	.0090	.00098
60	.0328	.2021	.0066	.00073
70	.0261	.1954	.0051	.00055
80	.0216	.1909	.0041	.00043
90	.0168	.1861	.0031	.00031
120	.0110	.1803	.0020	.00016

Figure 26

Plot of Log$\left[-\frac{d(a-x)}{dt}\right]$ Against Log$\left[(a-x)(b-x)\right]$ for the Reactions of Oleic Acid with Glycerol

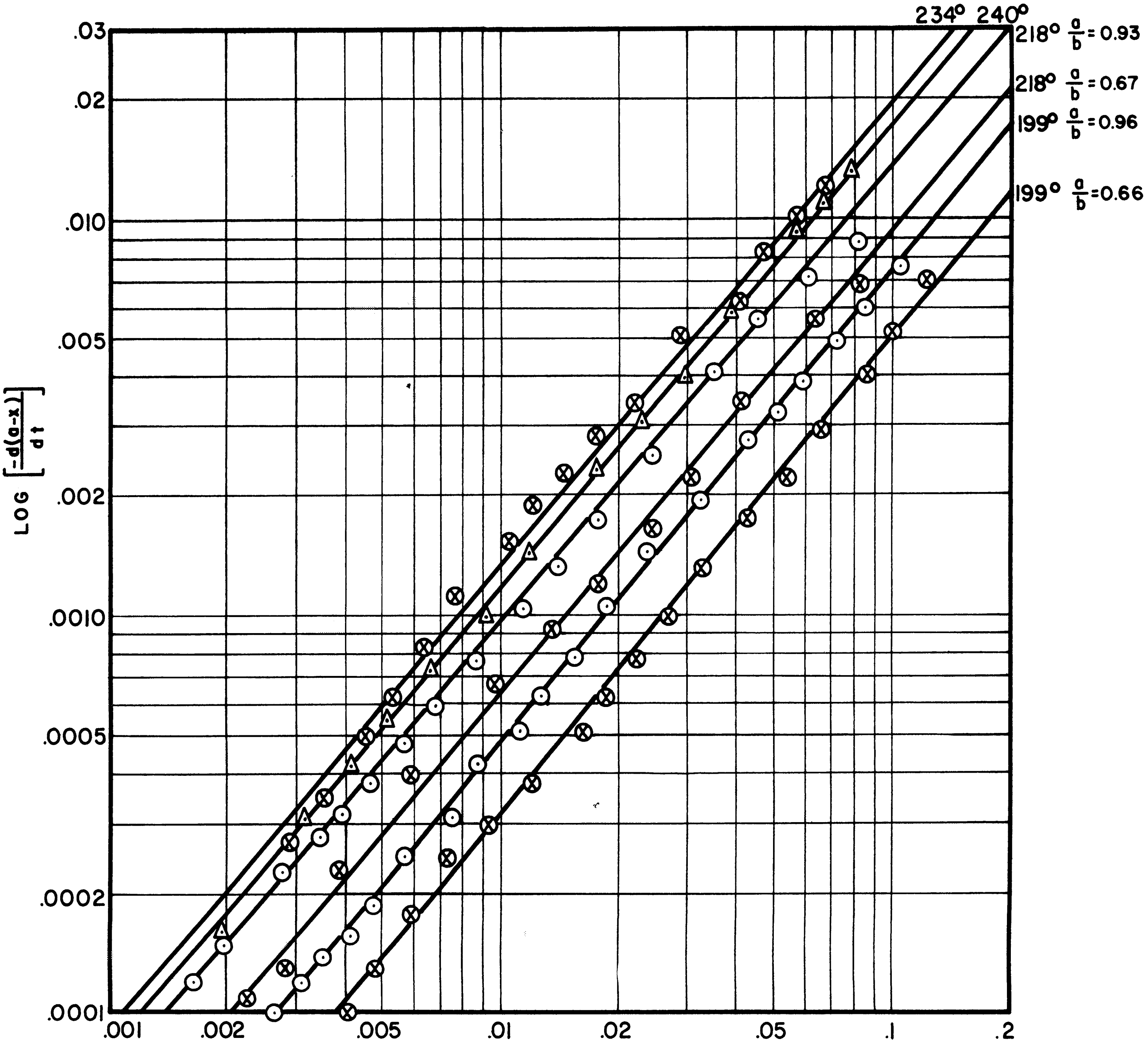


Table 26

Data on Reaction Between Linoleic Acid and Glycerol at 187°C

Time min.	(a-x) $\frac{\text{eq. Acid}}{\text{100 gm}}$	(b-x) $\frac{\text{eq. OH}}{\text{100 gm}}$	(a-x)(b-x)	$-\frac{d(a-x)}{dt}$ $\frac{\text{eq}}{\text{100 gm min}}$
0	0.3060	0.4624	0.1415	
5	.2890	.4454	.1287	0.00580
10	.2617	.4181	.1094	.00440
15	.2393	.3957	.0947	.00354
20	.2175	.3739	.0813	.00298
30	.1945	.3509	.0683	.00229
40	.1715	.3279	.0562	.00185
51	.1557	.3121	.0486	.00150
60	.1415	.2979	.0422	.00130
80	.1207	.2588	.0265	.00101
100	.1024	.2588	.0265	.00079
120	.0897	.2461	.0221	.00063
150	.0725	.2289	.0166	.00043
180	.0607	.2171	.0132	.00033
210	.0532	.2096	.0112	.00026
240	.0462	.2026	.0094	.00023
270	.0394	.1958	.0077	.00019

Table 27

Data on Reaction Between Linoleic Acid and Glycerol at 198°C

Time min.	(a-x) eq. Acid / 100 gm	(b-x) eq. OH / 100 gm	(a-x)(b-x)	$-\frac{d(a-x)}{dt}$ eq / 100 gm min
0	0.3214	0.3214	0.1033	
4	.2922	.2922	.0854	0.00804
8	.2632	.2632	.0693	.00617
11.8	.2469	.2469	.0610	.00463
16	.2298	.2298	.0528	.00388
20	.2165	.2165	.0469	.00335
25	.2006	.2006	.0402	.00288
30	.1884	.1884	.0355	.00247
40	.1665	.1665	.0277	.00194
50	.1524	.1524	.0232	.00157
60	.1390	.1390	.0193	.00128
70	.1274	.1274	.0162	.00106
80	.1156	.1156	.0134	.00088
100	.1019	.1019	.0104	.00063
120	.0893	.0893	.0080	.00048
150	.0771	.0771	.0059	.00034
180	.0671	.0671	.0045	.00025
210	.0600	.0600	.0036	.00019
240	.0541	.0541	.0029	.00015
300	.0449	.0449	.0020	.00009

Table 28

Data on Reaction Between Linoleic Acid and Glycerol at 202°C

Time min.	(a-x) $\frac{\text{eq. Acid}}{\text{100 gm}}$	(b-x) $\frac{\text{eq. OH}}{\text{100 gm}}$	(a-x)(b-x)	$-\frac{d(a-x)}{dt}$ $\frac{\text{eq}}{\text{100 gm min}}$
0	0.3235	0.3026	0.09789	
4	.2815	.2606	.07336	0.00800
8	.2583	.2374	.06132	.00630
12	.2326	.2117	.04924	.00474
16	.2209	.2000	.04418	.00387
20	.2097	.1888	.03959	.00325
25	.1950	.1741	.03395	.00271
30	.1823	.1614	.02942	.00234
35	.1693	.1484	.02512	.00205
40	.1626	.1417	.02304	.00181
50	.1466	.1257	.01843	.00144
60	.1345	.1136	.01528	.00116
70	.1255	.1046	.01313	.00097
80	.1132	.0923	.01045	.00082
100	.0997	.0788	.00785	.00058
120	.0860	.0651	.00561	.00043
150	.0761	.0552	.0042	.00026
180	.0690	.0481	.00332	.00019
210	.0653	.0444	.00290	.00015
240	.0602	.0393	.00237	.00013

Table 29

Data on Reaction Between Linoleic Acid and Glycerol at 208°C

Time min.	(a-x) $\frac{\text{eq. Acid}}{\text{100 gm}}$	(b-x) $\frac{\text{eq. OH}}{\text{100 gm}}$	(a-x)(b-x)	$-\frac{d(a-x)}{dt}$ $\frac{\text{eq}}{\text{100 gm min}}$
0	0.3214	0.3214	0.1033	
4	.2765	.2765	.0765	0.00935
8	.2461	.2461	.0606	.00702
12	.2238	.2238	.0501	.00555
16	.2026	.2026	.0411	.00432
20	.1885	.1885	.0355	.00358
25	.1726	.1726	.0298	.00300
30	.1591	.1591	.0253	.00252
40	.1375	.1375	.0189	.00186
50	.1216	.1216	.0148	.00140
60	.1110	.1110	.0123	.00109
70	.1026	.1026	.0105	.00088
80	.0922	.0922	.0085	.00074
100	.0796	.0796	.0063	.00055
120	.0683	.0683	.0047	.00042
150	.0592	.0592	.0035	.00030
180	.0503	.0503	.0025	.00020
210	.0445	.0445	.0020	.00014

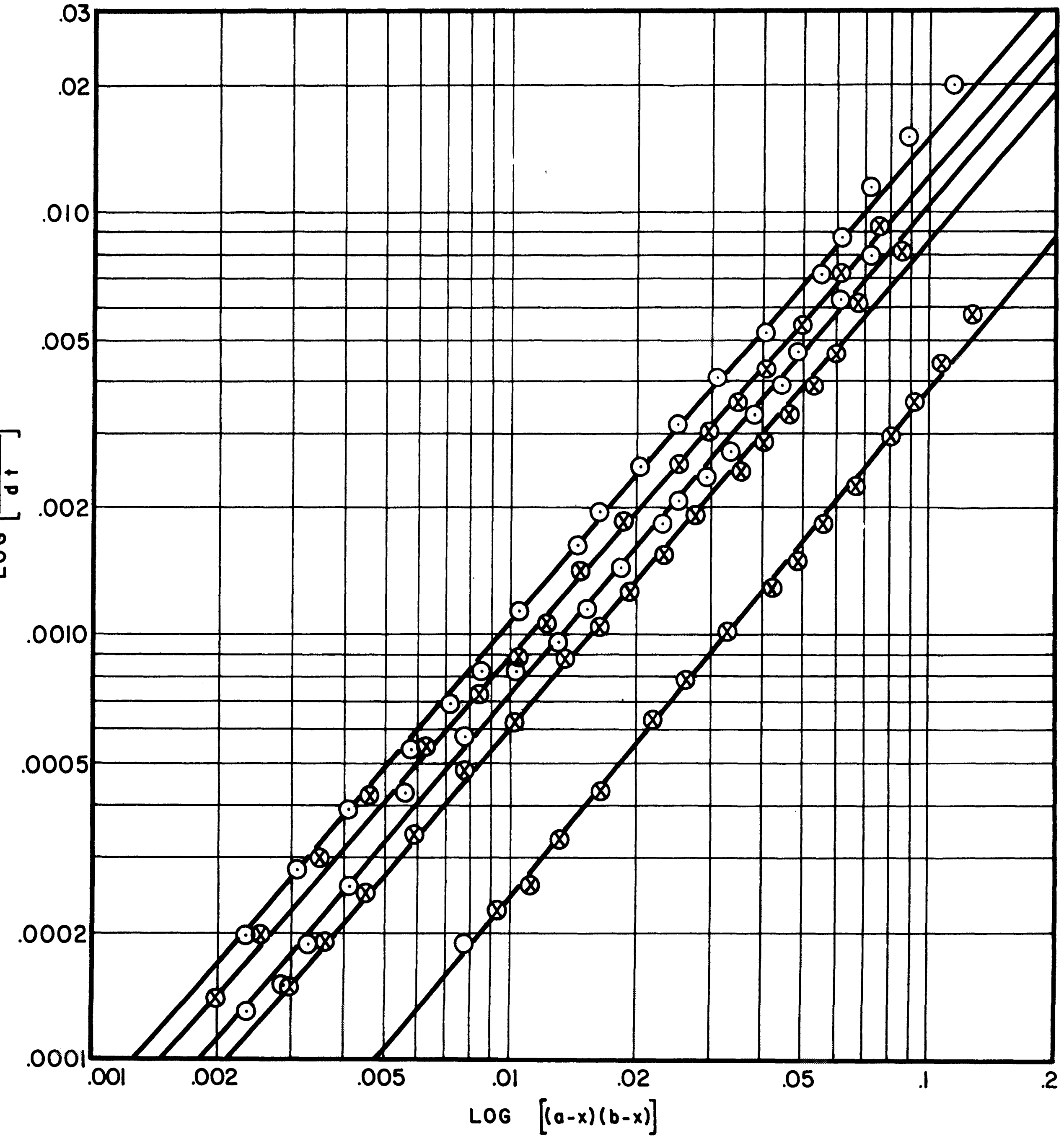
Table 30

Data on Reaction Between Linoleic Acid and Glycerol at 228°C

Time min.	(a-x) $\frac{\text{eq. Acid}}{\text{100 gm}}$	(b-x) $\frac{\text{eq. OH}}{\text{100 gm}}$	(a-x)(b-x)	$-\frac{d(a-x)}{dt}$ $\frac{\text{eq}}{\text{100 gm min}}$
0	0.3103	0.4232	0.1313	
2	.2851	.3980	.1134	0.02000
4	.2477	.3606	.0893	.01540
6	.2209	.3338	.0737	.01175
8	.1996	.3125	.0624	.00895
10	.1848	.2977	.0551	.00714
15	.1530	.2659	.0407	.00523
20	.1279	.2408	.0308	.00402
25	.1117	.2246	.0251	.00312
30	.0968	.2097	.0203	.00250
36	.0846	.1975	.0167	.00191
40	.0775	.1904	.0148	.00161
50	.0615	.1744	.0107	.00112
60	.0523	.1652	.0086	.00083
70	.0447	.1576	.0070	.00069
80	.0385	.1514	.0058	.00054
100	.0294	.1423	.0042	.00039
120	.0227	.1356	.0031	.00028
140	.0182	.1311	.0024	.00020

Figure 27

Plot of $\mathrm{Log}\left[-\frac{d(a-x)}{dt}\right]$ Against $\mathrm{Log}\left[(a-x)(b-x)\right]$ for the Reactions of Linoleic Acid with Glycerol.



APPENDIX D

Use of Least Squares Method for Evaluating Slopes and Intercepts

In evaluating the constants in the various equations used to represent the experimental data, it was desired to obtain the most probable or "best" values for these constants. These "best" values should then represent all of the data with a minimum average error or deviation.

From the theory of probability the Guassian law of error has been developed. This law states that the most probable value of a quantity derived from a number of experimental observations of equal precision is the value for which the sum of the squares of the deviations is a minimum. The deviation of this principle of least squares will not be presented here, since only the application of this principle is involved.

The equations involved in this work can all be represented by the following form:

$$y = m + m_o x \qquad \text{(D1)}$$

where y and x are experimentally determined quantities and m and m_o are unknown constants.

The deviation, D, of any one observed value of y from the most probable value of y calculated from the corresponding value of x is

$$D = m + m_o x - y \qquad \text{(D2)}$$

For n experimental observations the sum of the squares of the deviations must be a minimum. Thus:

$$\Sigma D^2 = D_1^2 + D_2^2 + \ldots + D_n^2 = \text{minimum} \qquad (D3)$$

Now since ΣD^2 is a function of m and m_o, which are unknown, its minimum corresponds to a zero value of the derivative of ΣD^2 with respect to m and also m_o. Therefore, with respect to m,

$$\frac{\partial(\Sigma D^2)}{\partial m} = 2\left[D_1 \frac{\partial D_1}{\partial m} ++ D_2 \frac{\partial D_2}{\partial m} + \ldots D_n \frac{\partial D_n}{\partial m} \right] = 0 \quad (D4)$$

and a similar expression may be written with respect to m_o. The terms $\frac{\partial D}{\partial m}$ and $\frac{\partial D}{\partial m_o}$ may be evaluated from Equation D 2.

It is seen that

$$\frac{\partial D}{\partial m} = 1$$

and

$$\frac{\partial(\Sigma D^2)}{\partial m} = 2(m + m_o x_1 - y_1 + \ldots + m + m_o x_n - y_n) = 0$$

$$(D5)$$

Similarly

$$\frac{\partial D}{\partial m_o} = x$$

and

$$\frac{\partial(\Sigma D^2)}{\partial m} = 2(m x_1 + m_o x_1^2 - x_1 y_1 + \ldots + m x_n + m_o x_n^2 - x_n y_n) = 0$$

$$(D6)$$

Equations D5 and D6 can now be written in summation form as follows:

$$\Sigma y = nm_o + m\Sigma x \qquad (D7)$$

$$\Sigma xy = m_o\Sigma x + m\Sigma x^2 \qquad (D8)$$

The solution of these two equations is

$$m_o = \frac{\Sigma y - m\Sigma x}{n} \qquad (D9)$$

$$m = \frac{\Sigma xy - m_o\Sigma x}{x^2} \qquad (D10)$$

Substituting for m_o in Equation D10 gives

$$m = \frac{\Sigma xy - \left(\frac{\Sigma y - m\Sigma x}{n}\right)\Sigma x}{x^2}$$

$$m = \frac{n\,\Sigma\,xy - y\Sigma\,x + m(\Sigma x)^2}{n\,\Sigma\,x^2}$$

Solving for m gives

$$m = \frac{n\Sigma xy - \Sigma y\Sigma x}{n\Sigma x^2 - (\Sigma x)^2} \qquad (D11)$$

and after m is known from Equation D11, m_o can be calculated from Equation D9.

These two equations, D9 and D11, can now be applied to evaluate the necessary slopes and intercepts desired.

Equation (10) is

$$-\frac{d(a-x)}{dt} = k\left(\frac{1}{b}\right)^{\gamma}\Big((a-x)(b-x)\Big)^{\alpha}, \qquad (10)$$

Taking logarithms of both sides yields:

$$\log -\frac{d(a-x)}{dt} = \log k\left(\frac{1}{b}\right)^{\gamma} + \alpha \log (a-x)(b-x)$$

This equation is now in the form

$$y = m_o + mx ,$$

so the method of least squares can be used to solve for α and $\log k(\frac{1}{b})^{\gamma}$ by substituting $\log\left[-\frac{d(a-x)}{dt}\right]$ for y, $\log k(\frac{1}{b})^{\gamma}$ for m_o, α for m, and $\log\left[(a-x)(b-x)\right]$ for x. Equation D11 now becomes

$$\alpha = \frac{n\Sigma \log\left[-\frac{d(a-x)}{dt}\right] \log\left[(a-x)(b-x)\right] - \Sigma \log\left[-\frac{d(a-x)}{dt}\right] \Sigma \log\left[(a-x)(b-x)\right]}{n\,\Sigma\left(\log\left[(a-x)(b-x)\right]\right)^2 - \left(\Sigma \log\left[(a-x)(b-x)\right]\right)^2}$$

and Equation D9 becomes

$$\log k(\frac{1}{b}) = \frac{\Sigma \log\left[-\frac{d(a-x)}{dt}\right] - \alpha\,\Sigma \log\left[(a-x)(b-x)\right]}{n}$$

The other application of this method was for the determination of the Activation Energies and the "Collision Factors" from the Arrhenius equation

$$k = Ae^{-E_o/RT}$$

Once again if logarithms are taken of both sides an equation of the proper form is obtained:

$$\log k = \log A - \frac{E_o}{2.303R}\left(\frac{1}{T}\right)$$

Proper substitution in equations D9 and D11 gives the solutions

$$\frac{-E_o}{2.303R} = \frac{n\,\Sigma \frac{1}{T}\log k - \Sigma \log k\,\Sigma\frac{1}{T}}{n\,\Sigma\left(\frac{1}{T}\right)^2 - \left(\Sigma\frac{1}{T}\right)^2}$$

$$\log A = \frac{\Sigma \log k + \frac{E_o}{2.303R}\Sigma\frac{1}{T}}{n}$$

APPENDIX E

Correlation of Northwestern Production Club Data (36) According to Equation 10.

The Northwestern Production Club (36) published data on the reaction between soybean oil fatty acids and diglycerol. They correlated the data in the same manner as Feuge, Kraemer, and Bailey (17). In this appendix their data is correlated according to equation 10, with γ being taken as unity.

The data was smoothed by the use of difference plots as described earlier and the instantaneous rates were obtained. Figure 28 represents a plot of $\log\left[-\frac{d(a-x)}{dt}\right]$ against $\log\left[(a-x)(b-x)\right]$. The slopes and intercepts of the straight lines obtained were evaluated and are listed in Table 31 under the headings of α and k respectively.

Table 31

Reaction Rate Constants for Data of Northwestern Production Club (36) When Correlated According to Equation 10 Assuming γ = 1.0.

Temp. °C	$\frac{a}{b}$	$\frac{1}{b}$	α	k
180	1.00	3.2113	1.19	0.0165
200	1.00	3.2113	1.13	.0296
220	1.00	3.2113	1.19	.0635
235	1.00	3.2113	1.19	.0880

The reaction rate constants were then tested to see if they obeyed the Arrhenius Equation. To do this a plot of log k against $\frac{1}{T}$ was made. The plot is represented by Figure 29 and it is seen that the rate constants obey the Arrhenius Equation. The Activation Energy, E_o, and "Collision Factor", A, were calculated and were found to be:

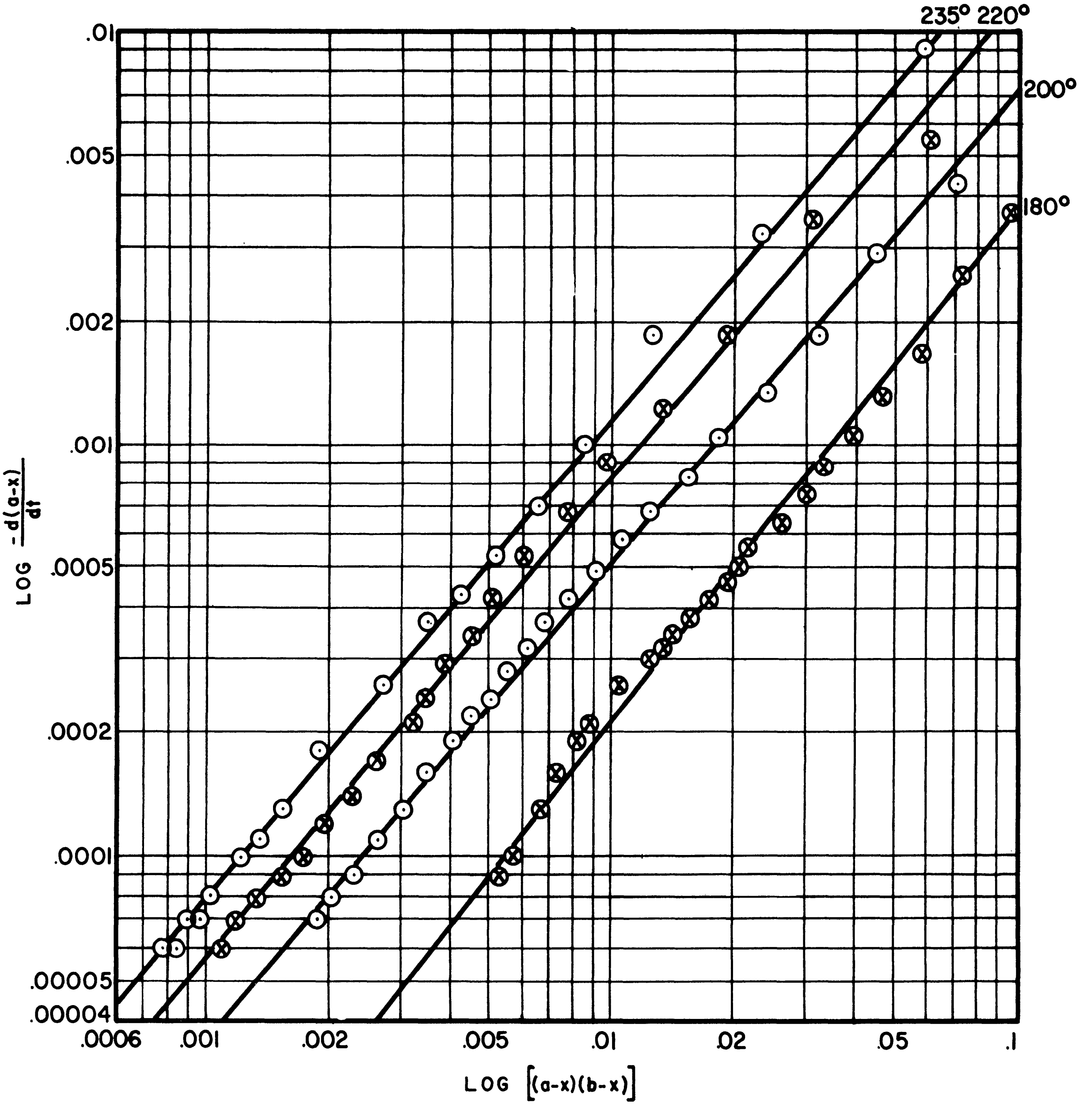
$$E_o = 14,300 \text{ cal/mole}$$

$$A = 1.34 \times 10^5$$

These values are in agreement with previous results.

Figure 28

Plot of $\mathrm{Log}\left[-\frac{d(a-x)}{dt}\right]$ Against $\mathrm{Log}\left[(a-x)(b-x)\right]$
Using Data of Northwestern Production Club (36)



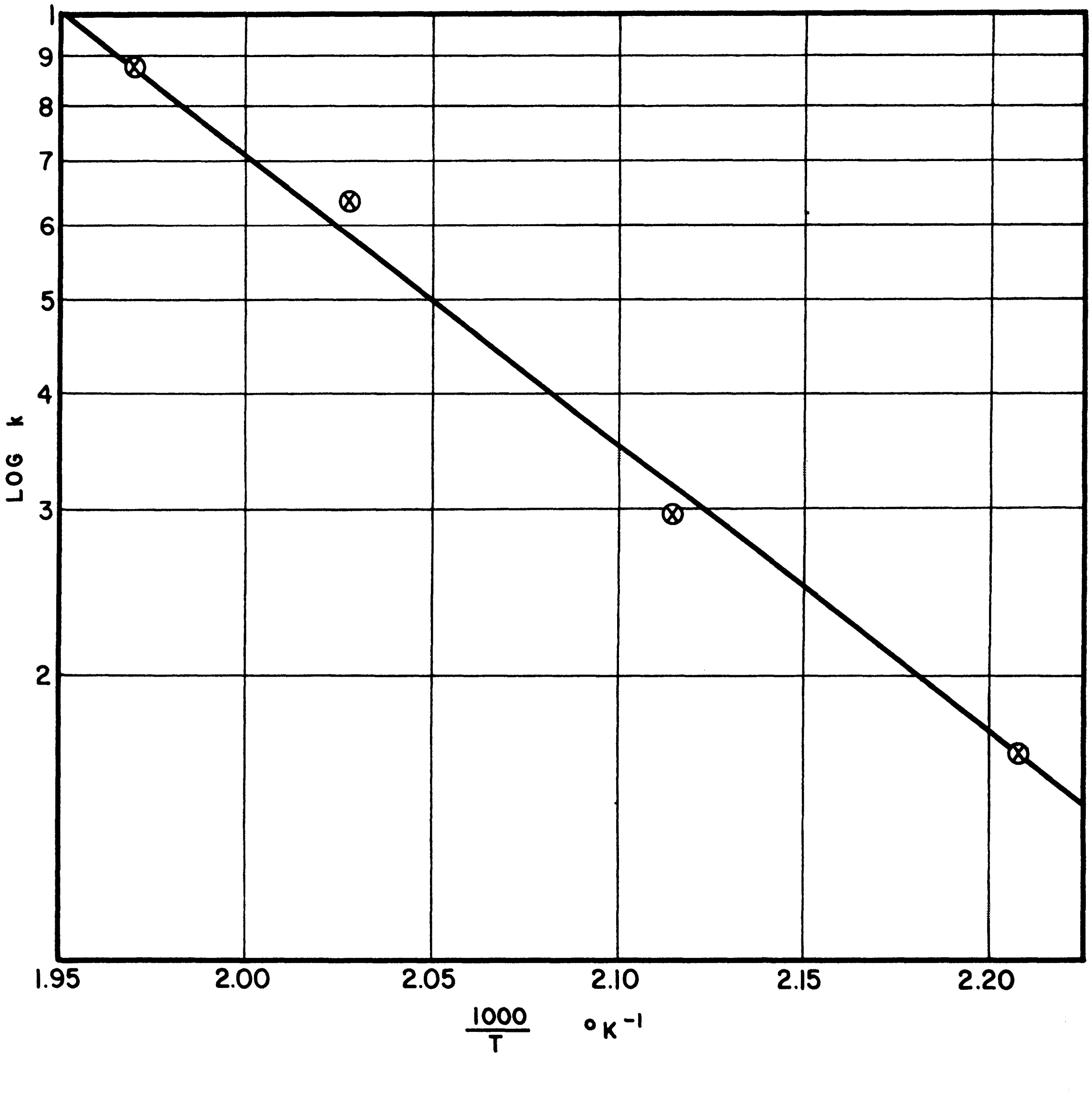


Figure 29

Plot of Log k Against $\frac{1}{T}$ from Data of Northwestern Production Club (36) as Calculated According to Equation 10.

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